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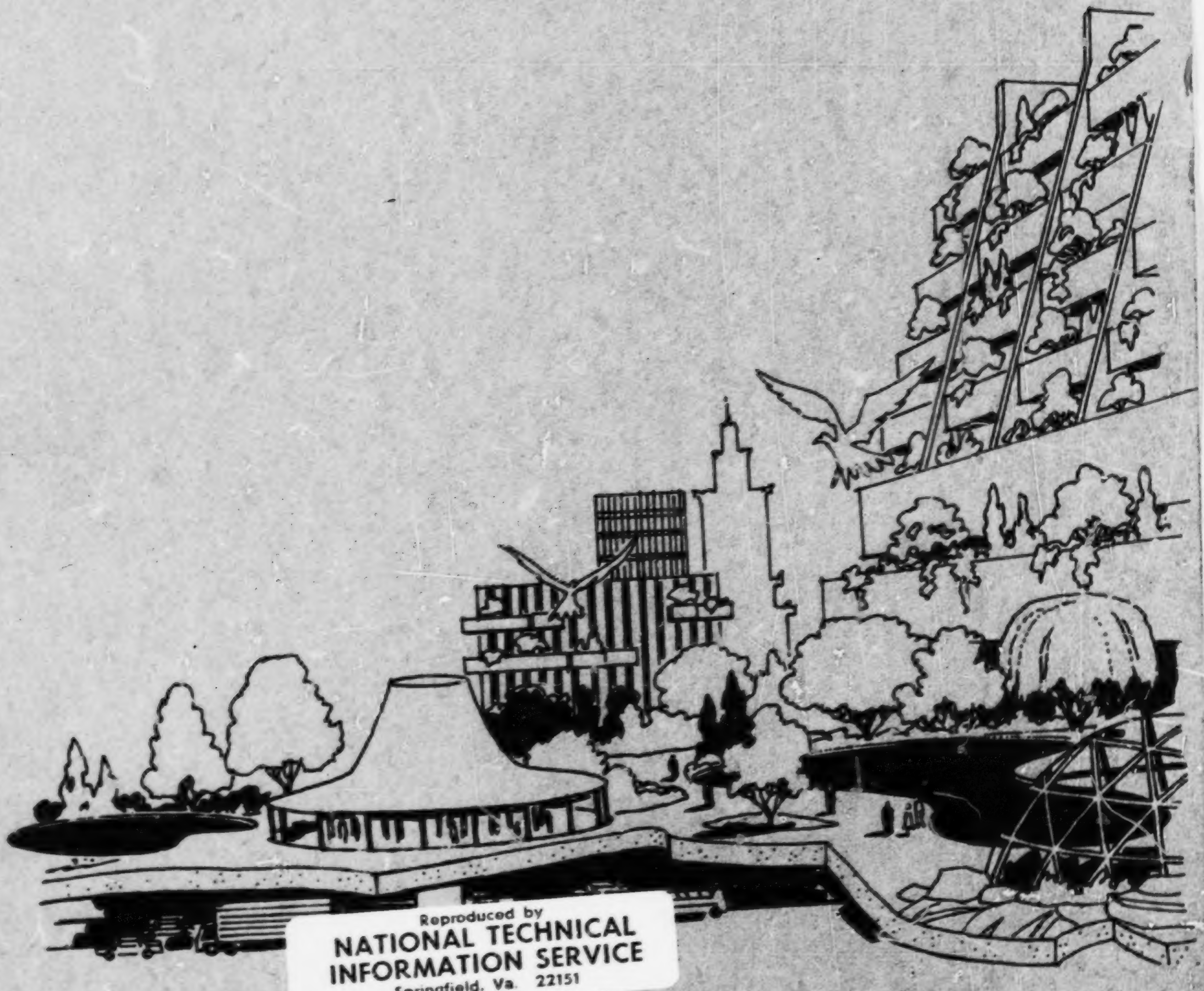
Development of Phosphate-Free Home Laundry Detergents



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27 Abstract

Basic studies were performed towards the development of phosphate-free home laundry detergents. Five surfactants were synthesized with the idea that they might possess hard ion chelating properties. The cleaning abilities of these materials were compared to the widely used linear alkylbenzene sulfonate as incorporated into the same formulations.

The detergent compositions contained 2% carboxymethylcellulose and the silicate content was varied. Sodium acetate and sodium carbonate were investigated as possible reservoirs of alkalinity. Surfactant compatibility with sodium chloride and sodium sulfate was examined. Other additives included trisodium nitrilotriacetate and sodium citrate at moderate levels. Fifteen detergent formulations were screened and the results leave little doubt that acceptable phosphate-free home laundry detergents can be developed. ~~(concise abstract)~~

( )

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by

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ABSTRACT

Basic studies were performed towards the development of phosphate-free home laundry detergents. A number of surfactants were synthesized for the purpose of incorporation into phosphate-free detergents. These surfactants were selected with the idea that they might possess hard ion chelating properties and/or be unaffected by hard water. The cleaning abilities of these materials were compared to those obtained with the same formulations containing a commonly used surfactant--namely, LAS.

In formulating these candidate surfactants, the loss of the functions of phosphates was compensated for by increasing the concentration of some of the common detergent builders and the use of other additives. The surfactants were formulated in compositions which, on a finished formulation basis, contained a carboxymethylcellulose concentration of 2%. The silicate content was varied but was most frequently used at levels above those which are currently employed. Sodium acetate and sodium carbonate were investigated as possible reservoirs of alkalinity. Surfactant compatibility with sodium chloride and sodium sulfate was also examined. Sodium citrate and trisodium nitrilotriacetate, at moderate concentration levels, were investigated for their value in combination with the surfactants.

During the course of the project, five surfactants were synthesized and fifteen detergent formulations were screened. The detergency data of these formulations were compared to the results obtained with a reference phosphate containing detergent which was supplied by the Association of Home Appliance Manufacturers (AHAM). Additionally, comparison was made to a local commercial brand.

A few basic formulations performed well at specific hardness levels under the test conditions employed and, while the testing did not evaluate all aspects of cleaning, the results leave little doubt that an acceptable phosphate-free home laundry detergent can be developed.

This report was submitted in fulfillment of Program No. 16080 DVF, Contract No. 14-12-575, under the sponsorship of the Federal Water Quality Administration.

Key Words: Detergents, algal control, formulation, surfactants, eutrophication, linear alkyl sulfonates, chelation, phosphates, organic compounds, water pollution control, phosphate-free detergents.

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CONCLUSIONS

The basic studies of this program indicate that a phosphate-free home laundry detergent can be prepared on a custom basis in which regional water hardness levels are considered. This can be accomplished through the use of specific anionic surfactants in combination with currently used builders and other readily available chemicals.

Selection of the anionic surfactant is dependent on wash water hardness. The three surfactants to be considered are sodium dodecylbenzenesulfonamidoethyl sulfate ($C_{12}H_{25}-C_6H_4-SO_2NHCH_2CH_2OSO_3Na$, IA), methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)propionate ($C_{12}H_{25}-C_6H_4-COCH(SO_3Na)CH_2CO_2CH_3$, II) and sodium dodecylbenzenesulfonate ($C_{12}H_{25}-C_6H_4-SO_3Na$, LAS). Surfactants IA and II can be built to give a hard water cleaning ability which is better than with LAS but do not show overall superiority when soft water performance is considered.

Carboxymethylcellulose (CMC), foam stabilizer and silicate were the three common detergent components which were retained in all formulations. A silicate content of 8-10% was determined to be the useful optimum range. Use of sodium acetate at concentrations which were equal to or greater than the acid equivalency of a 40% sodium tripolyphosphate content improved the detergency of the three surfactants but did not supply enough alkalinity to the wash water especially at the lower formulation concentrations. In the same vein, sodium carbonate is capable of raising the pH, but its use at high detergent concentration (10-40%) is detrimental to the anionic detergent formulations which were screened. All satisfactory formulations possessed sodium acetate; thus we have the following nuclear composition:

20% - Surfactant

2% - Carboxymethylcellulose

2% - Foam stabilizer

8-10% - Silicate

20-30% - Sodium acetate

(inert balance = water)

By itself, the preceding nuclear composition was found to be adequate in soft water (50 ppm) only when compound II or LAS was used as the surfactant. This same type of formulation was effective in moderately hard water (135 ppm) with either surfactants IA, II or LAS, the best overall performance being that which contained IA. (Though the LAS combination supplied the best cleaning ability in the normal use region of 0.25%, its poor low concentration effectiveness and decreased high concentration ability did not make it the best choice.) This same formulation containing IA, also showed good results in hard water (300 ppm), while the LAS containing composition placed a close second.

Addition of 15% sodium sulfate to the above basic formulation enhanced the effectiveness of the surfactant II composition which also gave good screening results at the 135 ppm hardness level. Similarly, in hard water, the sulfate containing formulation which possessed IA was good and about equal to that without sulfate, thus allowing for the inclusion of sodium sulfate as a "filler" component.

In combination with surfactant, CMC, foam stabilizer and silicate, trisodium nitrilotriacetate and sodium citrate were found to be of significant value only in hard water. Thus, the presence of these additives in soft water would seem to be unnecessary. The hard water detergency contribution by nitrilotriacetate is superior to that of citrate on an equal weight basis at a composition level of 16.8%. The addition of NTA to the aforementioned nuclear composition did not improve the overall effectiveness for any of the surfactants.

RECOMMENDATIONS

In order to develop the optimum composition(s) which can be intensively evaluated, the effects of a number of remaining factors must be determined. These factors fall into the general categories of (1) biological considerations, (2) ways to moderately increase wash water alkalinity, (3) evaluation of a select few additional additives, (4) test cloth variation in detergency screening, (5) soil anti-redeposition properties, and (6) optimization of the surfactant concentration as well as the surfactant hydrocarbon chain length.

Since the commercially unavailable surfactants, IA and II, are useful in phosphate-free compositions, it is mandatory that they be subjected to further biological testing before proceeding with development of formulations in which they might be incorporated. Aside from their performance in the confirming biodegradability test, the toxicities of these materials to snails, algae and fish should be determined by the 96-hour dynamic TLm.

A number of approaches can be taken to help increase the pH of the wash water. The most obvious is to increase the ratio of sodium oxide to silicon dioxide by using a different type of sodium silicate. Although this would probably be a successful solution to the problem, a higher sodium oxide content might be too caustic, requiring a hazardous warning label for the final formulation(s). Whereas a high sodium carbonate concentration is detrimental to the type of formulation which we have investigated, it is probable that smaller amounts of this material (2-4%) would raise the pH and allow for adequate performance. A novel approach to pH control might be accomplished through the use of small amounts of calcium hydroxide; this might also improve some compositions which performed poorly in soft water but reasonably well in hard water. The rationale for the use of calcium hydroxide is based on the fact that its water solubility decreases with increasing temperature and it possesses an inverse pH-temperature relationship. For example, a saturated aqueous solution of calcium hydroxide possesses a (buffered) pH of 13.4 at 0°C and 11.5 at 60°C while its water solubility is 0.185 g/100 ml at 0°C and 0.077 g/100 ml at 100°C. In hard water, the presence of calcium would help to suppress the solubility through the common ion effect on its solubility constant.

Of the many potential sequestering agents for which one can test detergent efficacy, tartrate, lactate and isethionate would be worthwhile for investigation due to their relative cheapness and biodegradability. These additives should be evaluated in combination with the different surfactants within the basic formulations.

The surfactant concentration should be kept constant (at 20%) while optimizing the other detergent components. Because test soils possess different cleaning characteristics, at least one other test cloth should be used for evaluations. At this time, we would recommend the use of the "EMPA" soiled cotton test cloth which is imported from Europe and is available through Testfabrics Inc. EMPA also has cloths which are available with various stains such as wine, blood, ink, milk and cocoa. In developing the finished formulation(s), a good cleaning ability is readily determined by the routine test procedure and infers an acceptable level of the soil anti-redeposition function; however, the detergent must be specially evaluated for this property under heavy soil loads to assure the fact that it possesses good all-around performance.

Optimization of the surfactant concentration might be best determined through critical micelle concentration studies since optimum cleaning results are usually achieved in the vicinity of this concentration region. These determinations would be performed on the surfactants with respect to their incorporation into formulations as well as in combination with single components and by themselves. In the best light this information could be utilized to assemble a chemical equivalency table which would serve the same type function as an isotonicity scale. Thus, the various detergent components would be rated as to their weight capabilities of contributing to the critical micelle concentration and can be related to a sodium tripolyphosphate sample.

Since there is usually an optimum in the relationship between hydrocarbon chain length and detergency, it would seem prudent to ascertain the effects of varying the chain length of at least one of the surfactants. The commercially available $C_{11.5}$-alkylbenzene, which was used to prepare the surfactants of this project, is the same which is used for the manufacture of LAS. The fact that an average $C_{11.5}$ hydrocarbon length is optimum for LAS does not necessarily confer optimum detergency in the different surfactant structures which have been prepared. A slightly lower chain length could optimize the detergent properties of the types of surfactants which have shown promise.

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SECTION I

INTRODUCTION

Eutrophication of the Nation's lakes has become a problem which is causing great concern to government and industry. Combined with other factors, the phosphates of detergents as well as fertilizers help to promote this eutrophication. Regardless of which condensed phosphate is used in detergents, the end product, which is discharged into the sewers, is that of ortho-phosphate. To exemplify the severity of the phosphate problem, one has only to consider the following approximate formulation which is typical of a high-sudsing laundry detergent:

20%	linear alkylbenzenesulfonate
40%	condensed phosphates
14%	sodium sulfate
4%	sodium silicate
2%	amide foam stabilizer
0.5%	sodium carboxymethylcellulose
19.5%	moisture and other minor components.

Thus, continued increase in the use of phosphate containing detergents due to elevated cleaning demands and an increase in the population will only serve to magnify a problem which is already severe. This report deals with an approach to the phosphate pollution problem--namely, th development of phosphate-free home laundry detergents.

Our approach departs from the present-day detergent technology which has developed over the past 25 years and in which two companies dominate the industry. The functions of phosphates in detergents can be briefly summarized as follows:

1. Chelation of calcium and magnesium ions
2. Lowering of the critical micelle concentration (cmc)
3. Soil suspension by deflocculation
4. Supply a reserve alkalinity at a buffered pH of 10 to 11.

Though other benefits are claimed for the phosphates, the above four are the most important ones. Since alkylbenzenesulfonates and fatty alcohol sulfates (the most popular surfactants used in the U. S.) are adversely affected by calcium and magnesium ions, the hard ion chelating function of phosphates allows for more efficient cleaning by these materials. Our work seeks to circumvent this problem by the use of surface active compounds which could possess self-chelating properties or which are not adversely affected by hard water. Thus, the candidate surfactants would differ in performance from commercially available surfactants insofar as the presence of calcium and magnesium would either enhance or have no tangible effect on their detergent action.

The phosphate detergency functions of soil deflocculation, alkalinity and lowering of the cmc would be compensated for by the use of other organic and/or inorganic salts. Conceivably, the lowering of the critical micelle concentration should be accomplished by the use of other electrolytes such as carbonates, sulfates or chlorides. The primary contribution to soil suspension is normally achieved through the use of carboxymethylcellulose (CMC) and the elimination of the phosphate contribution could be augmented by a concentration increase in this component. The final phosphate function, that of alkalinity reserve, should be served by carbonates and/or acetates.

This project then, consists of work in the areas of surfactant synthesis, surfactant biodegradability testing and formulation and evaluation of phosphate-free detergents.

SECTION II

SYNTHESIS OF THE SURFACTANTS

The candidate surfactants are representative of four types of surface active agents which might be self-chelating or unaffected by hard ions. The first surfactant class is the sulfated and sulfonated sulfonamides, represented by sodium dodecylbenzenesulfonamidoethyl sulfate ($C_{12}H_{25}$-C_6H_4-SO_2-$NHCH_2CH_2OSO_3Na$), sodium dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}$-C_6H_4-$SO_2NHCH_2CH_2SO_3Na$) and sodium N-methyl-dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}$-C_6H_4-$SO_2N(CH_3)CH_2CH_2SO_3Na$). The second class of surfactants, alkylaroyl(sulfo)propionates, is represented by methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)-propionate ($C_{12}H_{25}$-C_6H_4-$COCH(SO_3Na)CH_2CO_2CH_3$) while sodium 2-dodecylaminoethanesulfonate ($C_{12}H_{25}NHCH_2SO_3Na$) represents that of the amphoteric sulfonates. The final class is that of the ketosulfone carboxylates; both compounds involved here can be considered as levulinic acid derivatives. The first species is dodecyl 3-levulinate sulfone ($CH_3COCH(SO_2C_{12}H_{25})CH_2CO_2Na$) while the second is dodecyl 6-(4-keto)hexanoate sulfone ($C_{12}H_{25}SO_2CH_2CH_2COCH_2CH_2CO_2Na$). Although the preceding compounds are not necessarily new to the chemical literature, they are not in commercial production. The following discussion gives the pertinent synthetic information for these compounds. A more detailed discussion of the procedures and analyses is presented in the appendix.

Sulfated and Sulfonated Sulfonamides (Code No. I)

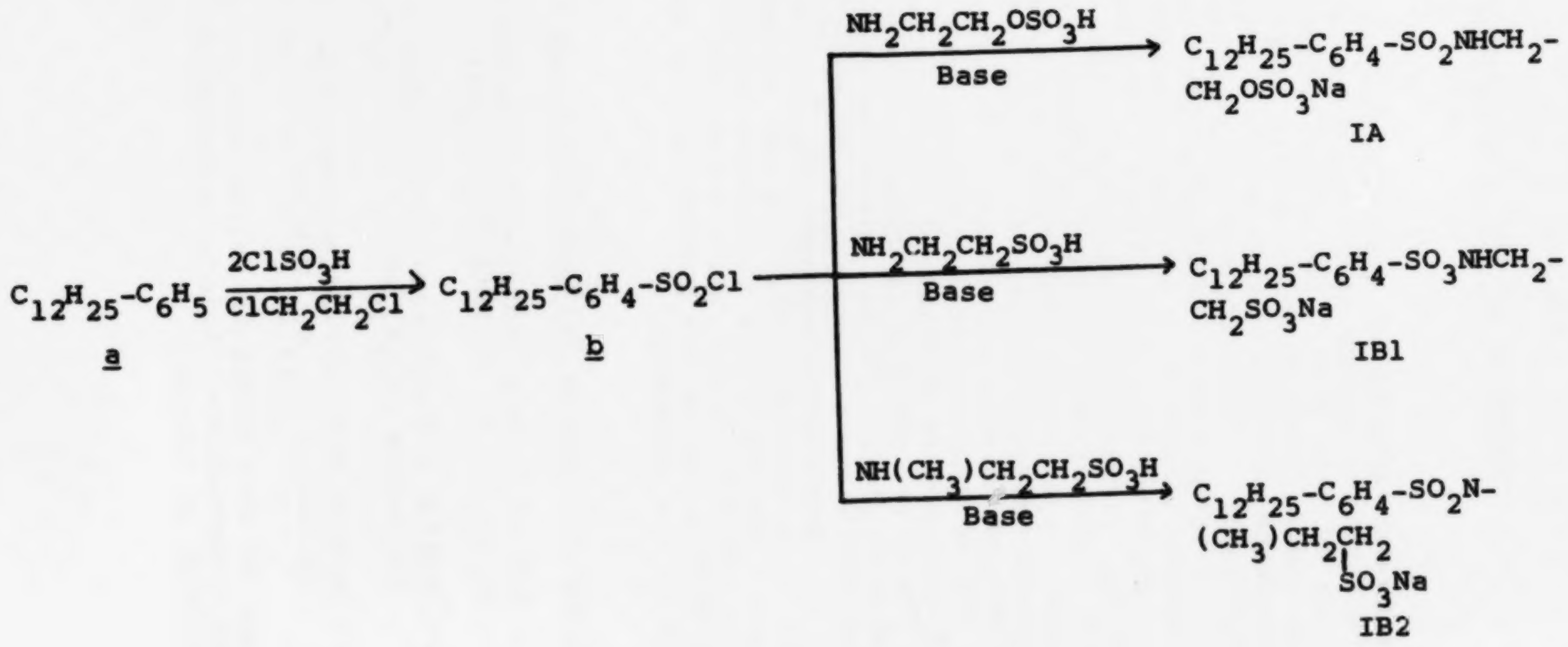
IA - Sodium Dodecylbenzenesulfonamidoethyl sulfate ($C_{12}H_{25}$-C_6H_4-$SO_2NHCH_2CH_2OSO_3Na$)

IB1 - Sodium Dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}$-C_6H_4-$SO_2NHCH_2CH_2SO_3Na$)

IB2 - Sodium N-Methyl-dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}$-C_6H_4-$SO_2N(CH_3)CH_2CH_2SO_3Na$)

All members of this class of surfactants were prepared from the common intermediate, dodecylbenzenesulfonyl chloride as illustrated in Scheme 1.

Scheme 1


$C_{12}H_{25}-C_6H_5$
a
$2ClSO_3H$
$ClCH_2CH_2Cl$
$C_{12}H_{25}-C_6H_4-SO_2Cl$
b
$NH_2CH_2CH_2OSO_3H$
Base
$C_{12}H_{25}-C_6H_4-SO_2NHCH_2-CH_2OSO_3Na$
IA
$NH_2CH_2CH_2SO_3H$
Base
$C_{12}H_{25}-C_6H_4-SO_3NHCH_2-CH_2SO_3Na$
IB1
$NH(CH_3)CH_2CH_2SO_3H$
Base
$C_{12}H_{25}-C_6H_4-SO_2N-(CH_3)CH_2CH_2SO_3Na$
IB2

The alkylbenzenesulfonylchloride (b) was prepared by adding the chlorosulfonic acid to a cooled solution of the alkylbenzene in 1,2-dichloroethane. After applying gentle aspiration, the crude solution was used "as is" in the reactions with aminoethyl hydrogen sulfate ($NH_2CH_2CH_2OSO_3H$), taurine ($NH_2CH_2CH_2SO_3H$), and N-methyltaurine ($NH(CH_3)CH_2$-CH_2SO_3H) to yield surfactants IA, IB1 and IB2 respectively. The dichloroethane solutions of b were added to aqueous mixtures of the reagents containing sodium bicarbonate. The reaction mixtures were maintained at a basic pH throughout the addition by the use of sodium bicarbonate as needed. After heating, the gelatinous product was precipitated by the addition of saturated potassium chloride solution, filtered by gravity and dried in a vacuum oven. The somewhat gummy products were extracted with hot solvent and the solvent was removed under reduced pressure to yield the product.

The dried products were titrated with a standard cation solution; the titrations indicated purities of 86%, 88% and >95% for compounds IA, IB1 and IB2 respectively. The qualitative features of the infrared and proton magnetic resonance spectra were acceptable for the assigned structures. A more detailed interpretation of the PMR spectra indicated a purity of 75% for IB1 and 80% IB2. A similar analysis was not possible for surfactant IA. The detailed titration and analytical data are presented in the appendix.

Alkylaroyl(sulfo)propionates (Code No. II)

II - Methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)-propionate ($C_{12}H_{25}$-C_6H_4-$COCH(SO_3Na)CH_2CO_2CH_3$)

The synthetic route to this surfactant[1] is shown in Scheme 2.

Scheme 2

$$\underset{\underline{a}}{C_{12}H_{25}\text{-}C_6H_5} \xrightarrow[\text{Anhyd. }AlCl_3]{\underline{\text{Maleic Anhydride}}} \underset{\underline{b}}{C_{12}H_{25}\text{-}C_6H_4\text{-COCH=CHCO}_2H}$$

$(ClCH_2CH_2Cl)$

Step 1

$$\xrightarrow[(ClCH_2CH_2Cl)]{CH_3OH/H^+/\text{Reflux}} \underset{\underline{c}}{C_{12}H_{25}\text{-}C_6H_4\text{-COCH=CHCO}_2CH_3}$$

Step 2

$$\xrightarrow[\text{Pressure}]{NaHSO_3/110\text{-}140°} \underset{\text{II}}{C_{12}H_{25}\text{-}C_6H_4\text{-}C_6H_4\text{-COCH(}SO_3Na\text{)}CH_2CO_2CH_3}$$

Step 3

The acylation by maleic anhydride (Step 1) was accomplished by adding the alkylbenzene (a) to the cooled mixture of maleic anhydride and aluminum chloride in dichloroethane. The reaction mixture was treated with a sulfuric acid-isopropyl alcohol solution and the upper organic layer was washed twice more with the acid-alcohol solution and then with saturated sodium chloride solution. The crude product was stripped of solvent under reduced pressure and yielded the intermediate acid (c). The IR and PMR spectra were in excellent agreement with the acrylic acid structure, b. PMR data and titration with standard base indicated good purity for this intermediate. This acid was redissolved in dichloroethane and esterified with methanol by azeotroping in the presence of sulfuric acid (Step 2). After removing the dichloroethane under reduced pressure, the residue was titrated with standard ethanolic potassium hydroxide solution. The acid content was less than 4%. PMR and IR data confirmed the esterification.

Conversion of the acrylate (c) to the desired product (II) was accomplished by the addition of sodium bisulfite across the alkene function (Step 3). This reaction was carried out in a Parr pressure reactor in the presence of water at 110-140°C. Titration of the final product by a standard cation solution indicated a purity of 90%, while PMR data showed the material to contain about 80% of the desired surfactant (II). A detailed interpretation of the analytical data is presented in the appendix. While the sodium sulfonato group is shown in a specific location within the molecular structure, the analytical data does not prove this assumption. The sulfonato group can, in fact, be in either the 2 or 3 position of the propionate nucleus.

Amphoteric Sulfonates (Code No. III)

IIIA - Sodium Dodecylaminoethanesulfonates ($C_{12}H_{25}NHCH_2CH_2SO_3Na$)

IIIB - Sodium N-Hydroxyethyl-2-dodecylaminoethanesulfonate ($C_{12}H_{25}N(CH_2CH_2OH)CH_2CH_2SO_3Na$)

The yield compound IIIA, as prepared in accordance with Scheme 3, was rather poor.

Scheme 3

$$\underset{\underline{a}}{C_{12}H_{25}NH_2} + \underset{\underline{b}}{HOCH_2CH_2SO_3Na} \xrightarrow[200\text{-}225^\circ]{\text{Pressure}} \underset{\text{IIIA}}{C_{12}H_{25}NHCH_2CH_2SO_3Na}$$

This surfactant possessed poor detergent properties and was dropped in the very early stages of screening.

Because of the poor detergent properties of the above parent molecule, surfactant IIIB was not prepared.

Ketosulfone Carboxylates (Code No. IV)

IVA - Dodecyl 3-Levulinate Sulfone ($CH_3COCH(SO_2C_{12}H_{25})CH_2CO_2Na$)

The proposed synthetic route to the levulinate, IVA is shown in Scheme 4.

Scheme 4

$$\underset{\underline{a}}{\mathrm{CH_3COCH_2CH_2CO_2H}} \xrightarrow[\text{Step 1}]{\mathrm{Br_2}} \underset{\underline{b}}{\mathrm{CH_3COCHBrCH_2CO_2H}} \xrightarrow[\text{Step 2}]{\mathrm{RS^-Na^+}}$$

$$\underset{\underline{c}}{\mathrm{CH_3COCH(SR)CH_2CO_2Na}} \xrightarrow[\text{Step 3}]{\text{Oxidation}} \mathrm{CH_3COCH(SO_2R)CH_2CO_2Na}$$

The bromination of levulinic acid in benzene (Step 1) supplied a product which contained three brominated isomers and a small amount of starting material. This product was found to be suitable for use in Step 2, where displacement of the bromo group by mercaptide yielded a product which was a mixture of two isomers, which included the desired intermediate, c.

A number of attempts were made to oxidize the mixture of thioethers to their sulfone derivatives as shown in Step 3 of Scheme 4. None of these experiments were successful in supplying the desired surfactant IVA. We were therefore unable to investigate the value of this type of surfactant in phosphate-free formulations.

SECTION III

SURFACTANT BIODEGRADABILITY

The biodegradabilities of surfactants IA, IB1, IB2 and II were determined by the presumptive (shake culture) test. A commercial sample of LAS was included as a control. Due to its amphoteric properties, surfactant IIIA did not lend itself to the spectrometric analysis of the procedure, however, its poor detergent properties obviated the need for this testing since it was eliminated as a candidate surfactant.

General Conditions for Degradability by Microorganisms[1]

Microorganisms are inoculated into flasks which contain a chemically defined microbial growth medium and the test surfactant. Aeration is accomplished by continuously shaking the flask. Biodegradation is determined by measuring the reduction in surfactant content during the 8-day test period which follows two 72-hour adaptive transfers. Samples were withdrawn from the flask on the seventh and eighth day as well as at the start of the test period. These samples were analyzed for anion content by the methylene blue method as generally described in the following section. The average value obtained from the seventh and eighth day samples were used to compute biodegradability. The microbial inoculum was obtained from the Metropolitan Sanitary District of Greater Chicago. The surfactant sample size was 30 mg/liter of culture medium.

According to this test, a surfactant is considered to be biodegradable if reduction equals or exceeds 90%. If surfactant reduction falls between 80% and 90% the results are inconclusive and the material must be evaluated by the confirming test before a conclusion can be reached. A value below 80% in the presumptive test classifies the material as not adequately biodegradable. Because we processed the samples immediately, the use of formaldehyde in the samples was unnecessary.

General Procedure for Anion Analysis by the Methylene[2] Blue Method

Alkylbenzenesulfonates (ABS), linear alkylbenzenesulfonates (LAS) and alkylsulfates form a blue, chloroform soluble salt with methylene blue. The intensity of the blue color is measured spectrophotometrically at the wavelength where the color intensity is proportional to the concentration of this salt. The optical density of the sample is then used to determine the anion content by reference to a calibration curve which was prepared with the specific surfactant.

The general procedure is as follows: The test sample is mixed with a stock solution of methylene blue. After allowing sufficient time for salt formation (1/2 hour) the acidifed solution is extracted with aliquots of chloroform. The combined chloroform extract is washed with an aqueous wash solution followed by backwashing of the aqueous layer with chloroform. The chloroform backwashings are combined with the original chloroform extracts. Finally, the chloroform solution is brought to volume (100 ml) after filtering through a pledget of glass wool.

Thus, a requisite for the use of this analytical procedure with our surfactants is that we obtain a straight line relationship between optical density and concentration at the wavelength of the analysis. The materials used as surfactants IA, IB1, IB2 and II possessed this requisite relationship. These reference calibrations are shown as a composite in Graph 1 of the appendix. Though more than one calibration was performed for each of the surfactants, the Graph 1 composite shows the calibration which possessed the least deviation from the straight line.

It is of interest to note that the tangents of the calibration lines for the surfactants generally decrease with increasing molecular weight of the anionic species. The theoretical molecular weights of the anions are: LAS = 325, IB1 = 432, II = 439, IA = 448 and IB2 = 446. In the case of IA vs IB2 where the molecular weight are almost equal, this relationship is reversed. This general trend would be expected if the color contribution came from the methylene blue cation. Thus, the lower the molecular weight of the anion, the more molecules per unit weight are available for the formation of the colored species. The ratios of the tangents for the calibration lines are crudely within 10% of the anionic molecular weights relative to LAS. The wavelength of 652 mμ was checked for each species involved and was found to be an acceptable region.

Results of Biodegradability Testing

The results of biodegradability testing are given in Table 1. Since the testing of IA and II was initiated on a different day than that of IB1 and IB2, the LAS control data consist of two sets of values corresponding to the IA, II and IB1, IB2 cycles.

All candidate surfactants show better than 85% biodegradability. It should be noted, however, that the LAS controls are at values which are somewhat less than those required for this species. This, of course, indicates that the degrading activity of the culture is somewhat less than what is normally expected.

Table 1

BIODEGRADABILITY OF SURFACTANTS BY THE PRESUMPTIVE TEST*

Sample Time (Days)	Surfactant Concentration Present in Culture (μg/ml)[a]		Biodegradability[b] (%)
	LAS[c] (Commercial Sample)		
	For IA and II	For IB1 and IB2	
0	26.8	25.0	
7	2.7	3.0	
8	1.6	2.4	91.8% 89.2%
	SURFACTANT IA		
0	33.2		
7	4.6		
8	3.8		87.3%
	SURFACTANT IB1		
0	25.8		
7	4.0		
8	3.2		86.0%
	SURFACTANT IB2		
0	31.5		
7	3.8		
8	3.6		88.3%
	SURFACTANT II		
0	25.5		
7	3.8		
8	3.6		85.5%

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*SOAP & DETERGENT ASSOCIATION, J. Am. Oil Chemists Soc., 42, 986 (1965); APHA, AWWA AND WPCF, STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTE WATER, p. 297, BOYD PRINTING CO., ALBANY, New York (1965).

[a] Values given are the average of two determinations using different sample sizes. The zero day sample value is derived from analysis of a 1 and 2 ml aliquot, while the 7 and 8 day determinations are derived from a 10 and 20 ml sample. The value supplied by the reference calibration was divided by the number of mls of inoculum used for the determination. Theoretical zero time concentration is 30 μg/ml.

[b] Calculated as percent removal using the found zero day concentration as the starting amount and the average of the 7th and 8th day values as the final concentration.

[c] Testing of IA and II was initiated on a different day from that of IB1 and IB2. LAS was included in each of the two test cycles; therefore two sets of values are given for this reference surfactant.

SECTION IV

DETERGENCY FORMULATIONS AND EVALUATIONS

Test Procedure[3,4]

The detergency evaluations were carried out by washing artificially soiled cloths in a Tergotometer which is a simulated washing machine manufactured by the U. S. Testing Co. This unit is the most convenient and practical from the standpoint of screening tests. Other mechanical devices, such as regular washing machines, would require too much input of time, personnel and material. In this procedure, three swatches of standard soiled cotton cloth (4 1/2 x 5") were placed in each of the four Tergotometer containers and the cloths were washed in solutions containing the detergent at 0.1, 0.2, 0.3 and 0.5% on a finished formulation basis. The fabrics were then washed at 150 rpm for 15 minutes at 120°F. The cleaned cloths were ironed after a 2-minute rinse cycle in the Tergotometer. The reflectance of the washed cloths was then compared to that of the soiled cloths using the green phototube of a Hunterlab Model D40 reflectometer which was standardized against a gray tile. In recording these readings, two right angle reflectance values were recorded for each cloth sample before and after washing. The average of the six readings (two for each of the three cloths per wash solution) was used to compute the percent soil removal according to the following equation:

$$PSR = (R_w - R_s / R_o - R_s) \times 100$$

where

PSR = Percent Soil Removal

R_w = Average reflectance of the washed fabric (average of 6 readings, 2 for each of 3 cloths)

R_s = Average reflectance of the unwashed soiled cloth

R_o = Reflectance of the unsoiled cloth (In the case of the U. S. Testing Co. soiled cotton cloth, this value is supplied with the control data for the lot).

Commercially, at least three standard soiled cotton cloths are available in the U. S.; two are American made and one is European made. Additionally, a great number of investigations have been reported in the literature on the very important parameter of soil composition for the test cloths. Thus, a number of standard soils have been developed and investigated as being more practical (or realistic) in their composition. The possible constituents of soils range from the use of iron compounds[5] and a clay-oleic acid combination[6] to the processing of vacuumed carpet dirt.[7] The U. S. Testing Co. soiled cotton cloth, which was used in our work, is not easily cleaned by distilled water and shows only a small variation in cleanability when washed by plain water at hardnesses of 50, 135 and 300 ppm. Although some preliminary testing was done on Testfabrics' (Inc.) soiled cotton cloth, the fact that distilled water cleaned it almost as well as the AHAM-2A reference detergent led us to prefer the U. S. Testing Co. cloth. Table 2 gives the data which illustrate the differences in cleanability between these two cloths. Because there were differences between some lots of the U. S. Testing Co. cloth, the AHAM-2A formulation and a commercial product were tested in duplicate on each new lot of this cloth. Thus, on the basis of a reference, one could compare the results of tests which were obtained from different lots of cloth.

Table 2

PERCENT SOIL REMOVAL FROM SOILED COTTON CLOTHS BY WATERS OF VARYING HARDNESS

	% Soil Removal at Given Water Hardness (ppm as $CaCO_3$)			
	0	50	135	300
U. S. Testing Co.	9.8%	8.7%	8.1%	8.2%
Testfabrics Inc.	57.8%	32.0%	24.2%	20.3%

Formulations

The following composition is typical of a high-sudsing, phosphate containing laundry detergent:

20% Linear alkylbenzenesulfonate (LAS)

40% Sodium tripolyphosphate

6%	Sodium silicate
2%	Amide foam stabilizer
0.5%	Carboxymethylcellulose (CMC)
14%	Sodium sulfate
19.5%	Moisture and other inorganic components.

It should be noted that the above formulation excludes the consideration of brighteners, bleaches and/or enzymes which are present in a number of today's products.

Since the objective of this project is to develop an efficient phosphate-free home laundry detergent, one must compare the effectiveness of our formulations to that of a comparable phosphate-containing detergent. The Association of Home Appliance Manufacturers (AHAM) supplied a quantity of a phosphate containing reference standard detergent (No. 2A). The concentrations of the primary ingredients of this detergent are as follows:

13%	LAS
2%	Fatty acid
2%	Nonionic surfactant
1%	Carboxymethylcellulose
6%	Sodium silicate
47.5%	Sodium tripolyphosphate (analyzed as 27.5% phosphorous pentoxide).

The absence of a foam stabilizer and the presence of fatty acid in this formulation make it a low sudsing detergent. This AHAM-2A detergent was used as a reference formulation throughout our work. In addition, a local commercial product was also used as a control and for comparative purposes.

Table 3 lists the components and percent composition for each formulation investigated ("A" through "O"). Each Test Formulation (TF) is comprised of a small series obtained by using different surfactants. For example, use of LAS and surfactants IA, IB1, IB2, II and IIIA within Test Formulation "A" (TF A), at the 20% concentration specified, yields the "A" series which is comprised of 6 members, designated as TF A-LAS, TF A-IA, TF A-IB1, TF A-IB2, TF A-II and TF A-IIIA, respectively. The

Table 3

% COMPOSITIONS OF TEST FORMULATIONS
(Finished Formulation Basis)

Component	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Carboxymethylcellulose	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Cocodiethanolamide	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sodium Silicate	(10.1)	(10.1)	(10.1)	(2.8)	(10.1)	(10.1)	(14.1)	(10.1)	(10.1)	(10.1)	(10.1)	(10.1)	(8.4)	(8.4)	(8.4)
SiO_2	7.2	7.2	7.2	2.0	7.2	7.2	10.1	7.2	7.2	7.2	7.2	7.2	6.0	6.0	6.0
Na_2O	2.9	2.9	2.9	0.8	2.9	2.9	4.0	2.9	2.9	2.9	2.9	2.9	2.4	2.4	2.4
Sodium Acetate	-	22.2	-	30.0	30.0	-	-	-	-	30.0	22.2	-	20.0	20.0	30.0
Trisodium Nitrilotriacetate	-	-	-	-	-	16.8	-	-	-	16.8	16.8	-	-	-	16.8
Sodium Carbonate	-	-	40.0	-	-	-	-	-	-	-	-	-	-	10.0	-
Sodium Chloride	-	-	-	-	-	-	-	10.0	-	-	-	-	-	-	10.0
Sodium Sulfate	-	15.0	-	-	-	-	-	-	10.0	-	-	-	-	-	-
Sodium Citrate	-	-	-	-	-	-	-	-	-	-	-	16.8	-	-	-
Surfactant	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Other (H_2O)	65.9	28.7	25.9	43.2	35.9	49.1	61.9	55.9	55.9	19.1	26.9	49.1	47.6	37.6	10.0

following list gives the sources and grades for the formulation components of Table 3.

Component	Source	Specifications
Carboxymethylcellulose	Hercules Inc.	Type 7LT
Cocodiethanolamide	Stepan Chemical Co.	Ninol 128 extra
Sodium silicate	Philadelphia Quartz Co.	Solution, star grade
Sodium acetate	Celanese Chemical Co. (also B&A)	Technical Anhyd, reagent
Trisodium Nitrilotriacetate	Hampshire Chemical Co.	NTA $Na_3 \cdot H_2O$
Sodium carbonate	B&A	Anhyd, reagent
Sodium chloride	B&A	Crystals, reagent
Sodium sulfate	B&A	Anhyd, reagent
Sodium citrate	B&A	Crystals, reagent
Linear Alkylbenzenesulfonate	Conoco	Slurry, C560

The sodium silicate solution and LAS slurry were used in quantities which accommodated for their analyses to yield the active ingredient concentrations shown in Table 3. The nitrilotriacetate concentrations shown in Table 3 are exclusive of the water of hydration (16.8% NTA Na_3 = 18.0% NTA $Na_3 \cdot H_2O$).

It is seen that all of our Test Formulations contain carboxymethylcellulose (CMC), cocodiethanolamide and sodium silicate. In order to accommodate for some loss in soil-suspending properties due to the elimination of phosphate, the levels of CMC are higher than those usually employed which is also true in most cases for sodium silicate. The surfactant concentration is at the high of the normal use level, while the foam stabilizer, cocodiethanolamide, is present at a normal concentration. Each formulation was tested in waters of 50, 135 and 300 ppm hardness. The 50 ppm water was prepared from calcium and magnesium chlorides using distilled water. Since Chicago tap water possesses an approximate hardness of 135 ppm, it was used directly for this level. The 300 ppm water was prepared by adding calcium and magnesium chlorides to Chicago tap water.

Test Results and Discussion

In considering the data and discussions which follow, it must be kept in mind that the previously described detergency evaluation procedure was employed as a tool to aid in developing and evaluating a detergent. The efficiency and economics of this test method make it one of the best choices for our work.

Graphic form of the data is presented in the appendix showing four-point detergency curve composites which include the AHAM-2A and commercial product detergency curves for the batch of cloth on which testing was performed. The results of testing are interpreted and discussed on a comparative basis using the commercial brand and AHAM-2A as internal reference curves.

In comparing the results of our detergency screening (graphs 2 through 46, appended), it is seen that the AHAM-2A formulation is quite inferior to the commercial brand tested. In fact, superiority to AHAM-2A was readily achieved by a number of formulations at the different hardness levels. The most desirable detergency curve characteristics are best illustrated by those obtained from the commercial brand detergent where the low concentration (0.1%) cleaning ability is rather good with a near maximum cleaning ability being attained in the mid-concentration region of 0.25%. Further significant increases in formulation concentration (to 0.5%) produces only a nominal improvement in cleaning properties. Surfactant IIIA showed very poor detergent properties and was eliminated as a candidate at an early stage in testing. Surfactant IB2 was consistently inferior to its homolog, IB1 and was therefore eliminated from consideration at a somewhat later stage.

The composition of Test Formulation A allowed for evaluation of the surfactants' cleaning abilities in combination with some common builders and served as a backbone in testing other candidate components. To augment the loss in soil anti-redeposition properties created by the elimination of phosphates, the carboxymethylcellulose and silicate concentrations of TF A are at higher levels than those normally employed. The behavior of LAS (as combined in TF A) is typical for surfactants adversely affected by water hardness (Graphs 2-4). Whereas it displays the best cleaning ability in soft water (50 ppm), its efficiency in hard water drops considerably more than that observed for the phosphate-containing standards. Irrespective of concentration behavior, TF A-LAS still attains maximum detergencies which are among the best for the Formulation A series. While no other surfactant "A" formulation approaches LAS at 50 ppm, on the basis of overall behavior, surfactant II exhibits equivalency to LAS at 135 ppm while IB1 (and IIIA which was later dropped) is superior to LAS at the initial and mid-region concentrations in hard water (300 ppm).

A further increase in silicate from the 10.1% level in TF A to 14.1% in TF G (Graphs 20-22) was detrimental to cleaning in soft water but generally enhanced the detergencies in the harder waters. This improvement was pronounced in the case of surfactant II at 135 ppm where the cleaning ability of TF G-II was equivalent to the brand detergent in the range of 0.28-0.5%. Although the cleaning by TF G-IA in 135 and 300 ppm water at 0.1% concentration was at a fair level, the remaining overall detergency was only equivalent to the LAS-containing formulation.

Formulations H and I (Graphs 23-28) are of the same basic composition as "A" but, in addition, contain 10% of sodium chloride and sodium sulfate, respectively. These "filler" ingredients were used in this manner to make sure that they presented no unexpected incompatibilities with the surfactants. It should be noted that the TF I series was screened on a batch of soiled cloth which possessed cleaning characteristics different than that used for Formulations "A" through "H". (This exemplifies the need for running reference standards on cloths which possess different cleaning characteristics.) While both chemicals slightly reduced the effectiveness of LAS in soft water, sodium sulfate (TF I) imparted a small improvement to the IA containing formula; additionally, TF H and TF I shows a drop in effectiveness at higher concentration, thus creating a maximum in the detergency curves. In the case of the sulfate formulation this latter characteristic is present to a somewhat lesser degree at 135 ppm but does not exist in 300 ppm wash water. On the other hand, the sodium chloride formulation ("H") loses this characteristic at 135 ppm hardness. Specifically, compounds II, IA and LAS behaved best with sodium chloride in 135 ppm water while sodium sulfate was better for surfactants IB1 and IA at 300 ppm. In both of the above situations, the formulations were superior to AHAM and approximated the results obtained with the commercial brand. At this point then, it was apparent that surfactants IA and IB1 were capable of functioning better than LAS in hard water (300 ppm).

Sodium carbonate and sodium acetate were investigated as possible alkaline builders to help replace the alkalinity lost by the elimination of phosphate. Addition of 40% sodium carbonate to TF A supplied Formulation C (Graphs 8-10). The 40% concentration of sodium carbonate was such that the calcium carbonate solubility constant (K_{sp}) was exceeded at all test levels. At 50 ppm hardness, the carbonate generally improved the performance of surfactants IA, IB1 and IB2 to a point where they were equal to AHAM in the 0.3% concentration region; although TF C-LAS did not possess as good a cleaning power at 0.25% as its TF A analog, the detergency curve showed a steadily increasing response to concentration, reaching the same maximum but at the 0.5% level. In harder waters, carbonate was detrimental to the cleaning ability of surfactant II, but significantly improved the effectiveness of IA at 135 ppm and LAS at 300 ppm. Of significant value is the fact that sodium carbonate improved the detergency of all the surfactants at the 0.1% formulation level in water of 300 ppm hardness.

The base, sodium acetate, was added to TF A at the 30% level to yield Test Formulation E (Graphs 14-16). While this move did not change the soft water detergencies of LAS and II, those of IA and IB1 were significantly improved. The net result was that IA, IB1, IB2 and II were roughly comparable to each other (approximating that of AHAM) while LAS was significantly better in the normal use region of 0.25% but dropped appreciably at higher concentration. Except for LAS, the use of sodium acetate greatly improved the cleaning levels at 0.1% for all members of the series over the entire range of water hardness. Cleaning results in moderately hard and hard water were excellent as compared to TF A. The best performer in 135 ppm water was surfactant II whose effectiveness is equivalent to the commercial product at 0.25% and above; though the effects of IA and IB1 were improved considerably, neither was superior to the LAS-containing formula. The results in hard water were the most dramatic with E-IB1 and E-II outperforming E-LAS while approximating the cleaning ability of the brand tested. Virtually all members of the TF E series surpassed the ability of AHAM at 135 and 300 ppm.

In seeking a complementary substitute for the hard ion effects of phosphate, trisodium nitrilotriacetate (NTA) and sodium citrate were screened for their chelating value in detergents. In addition to the composition of Formulation A, Test Formulation F contains 16.8% of NTA (Graphs 17-19). At 50 ppm the effect of NTA was to raise the effectiveness and improve the general curve characteristics for all members of the series. (The maximum cleaning ability of the LAS formulation was actually less than A-LAS but the general features of the data curve showed improvement.) In this case IA, II and LAS were almost equivalent and about equal to AHAM while IB1 (and IB2) was of somewhat reduced effectiveness. Performance by the "F" series in Chicago water was somewhat disappointing where the overall tendency was to reduce detergency characteristics. This was especially true for LAS. Thus, the effects of adding 16.8% of NTA were mixed. At 300 ppm, the top cleaning levels were increased in most instances but maxima appeared in the detergency curves as the cleaning ability dropped off at the higher concentration.

The results with Test Formulation L, containing 16.8% sodium citrate, were very poor at the 50 and 135 ppm hardness levels (Graphs 35-37). In all of these cases the cleaning abilities were drastically curtailed. In water of 300 ppm hardness, detergency levels were better than TF A in the mid-range of concentration, being roughly equivalent to the NTA-containing series, but the effectiveness was reduced at increased concentration.

The relative effects obtained by varying the components as discussed above are presented in Table 4.

The data obtained with Formulations "D" (Graphs 11-13) are the result of drastically reducing the silicate content of "E" to 2.8% while Formulations in the "M" series are derived from a simultaneous acetate and moderate silicate reduction. The results of screening for TF D and M (Graphs 11-13 and 38-40 respectively) will be discussed in terms of comparison to the TF E series which was superior to the A formulations. In comparing the detergency curves of Test Formulations D and E to those of "M" we must consider the fact that the soiled cloth used for the testing of "M" possessed different cleaning characteristics. Thus, all comparisons between the former and latter formulations must be made with respect to the reference standards ("Brand" and AHAM).

A drastic decrease in the silicate content of "E" to 2.8% (from 10.1%) gave the TF D series. In soft water, the only significant effect was an increase in the cleaning ability of the II containing formula. In Chicago water (135 ppm), none of the surfactant-D formulations showed any change as compared to the "E" analogs. There were also no significant differences between the two formulations at the 300 ppm hardness level.

As compared to the Formulation E series, the "M" series possessed only a slight silicate reduction, being 8.4%, while sodium acetate has been reduced to 20% (from 30%). All members of the TF M series were poorer than "E" at the 50 ppm level. M-LAS, IA and II showed good performances in Chicago water, being equal to, or possibly better than the

Table 4

INDIVIDUAL EFFECTS[a] OF VARIOUS BUILDERS AND ADDITIVES[b,c]

Surfactant	Hardness	Sodium Silicate (G)	Sodium Chloride (H)	Sodium Sulfate (I)	Sodium Carbonate (C)	Sodium Acetate (E)	Trisodium NTA (F)	Trisodium Citrate (L)
LAS	50	-	-	-	(+)		-	----
	135		+	-	(+)		-	---
	300	(+)		(+)	++	+	++	(+)
IA	50	-	-	(+)	+	+	++	---
	135	+	+	(+)	++	++		--
	300	++		+	+	++	++	(+)
IB1	50	-	-	-	+	+	+	---
	135	+	+	+	+	+	(-)	--
	300	-		+		++	+	(++)
II	50	-	-	-	+		++	---
	135	++	++	-	-	+++	(-)	--
	300	+++	++		-	+++	+++	+++

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[a] On a comparative basis to the "A" Formulation which contains the same surfactant.

[b] Blank space indicates "no effect".

[c] Parenthesized effects indicate a questionable result which could only be derived from one facet of the curve analysis.

brand used for reference; while M-LAS and II reached higher cleaning levels, they dropped in effectiveness at higher concentration, creating the condition of a maximum in their detergency curves. In the hardest water, reduction of acetate was highly detrimental to the IB1 and II containing "M" formulations. It should be noted here that the detergency curve of M-II at 300 ppm does not reach a discernible inflection over the range of concentration but rises steadily to attain a good detergency at 0.5% concentration.

No one member of the ten series of compositions discussed to this point shows an overall superiority. Thus, the best performers in soft water are apparently D-II and E-LAS. The cleaning ability of these formulations at the 0.25 - 0.3% concentration level approximates that of the reference brand and is far superior to AHAM. While their effectiveness tapers off at higher concentration, they are equal to each other and on a par with AHAM. At a 0.1% formulation concentration E-LAS performs poorly, being well below AHAM while D-II is equivalent to AHAM at this concentration. Choosing the best performers in water of 135 ppm hardness at this point is not an easy decision. The best results in the normally used concentration region of 0.25% were obtained with M-LAS which was superior to the reference brand at this point. Use of M-LAS at higher concentration showed a decrease in effectiveness from the maximum at 0.3%, dropping somewhat below the commercial product. At low concentration, its effectiveness was not very good although it was on a par with AHAM. The performance of M-II was very similar to M-LAS in Chicago water, its low concentration effectiveness being somewhat higher with maximum cleaning at 0.3% being somewhat inferior to M-LAS. While almost all "D" formulations and some "E" formulations were quite good, the best overall performer in moderately hard water seems to be M-IA; its low concentration effectiveness was the best and, while it did not possess the best cleaning ability at the 0.3% level, it was equivalent to the "brand" at this point; as opposed to a decreased detergency at higher concentration, it improved slightly, remaining roughly equivalent to the commercial brand. All members of the D, E and M series performed better than AHAM at 300 ppm hardness. Up to the highest concentration, M-IA, which appears to be the best at 300 ppm, performed better than any other member of the M series. At high concentration M-LAS was somewhat better. D-II, D-LAS, E-IB1 and E-II all possessed detergency properties which were about equivalent and on a par with the "brand" detergent.

The formulations discussed in the following dialogue are the result of combining the various additives whose functions help to replace those lost by the elimination of phosphate.

A slight reduction in the silicate content of "A" as well as the inclusion of 20% sodium acetate and 10% sodium carbonate leads to Formulation N (Graphs 41-43). All members of this series showed poor detergencies in soft water. In Chicago water, N-LAS and N-II possessed good cleaning ability up to 0.25% concentration which dropped sharply at higher concentration. This was also true of N-IA and N-IB1 in hard water where N-LAS showed good detergency only at the 0.25% concentration level. Overall, the Formulation "N" series showed no improvement over the best of those already discussed.

Formulations J, K and O (Graphs 29-34 and 44-46) are similar inasmuch as they all possess sodium acetate and NTA. Formulation J is obtained by the addition of 16.8% of NTA to the 30% acetate formulation ("E") while "K" is the same as "J" except that the acetate concentration has been reduced. Multiple comparisons of the data lead to a number of conclusions. By comparing the detergencies of Formulations J and K it is evident that in soft and moderately hard water the reduction of acetate in these NTA-containing formulas is detrimental to the cleaning ability, irrespective of the surfactant used. An additional favorable point for the use of higher acetate concentration in soft water is the fact that there was no drop in detergency at higher concentrations. In all cases except one, the results of acetate reduction showed no change in hard water; the lone exception was the J-IA, K-IA comparison which showed improvement upon reduction of the acetate.

At 50 ppm hardness, the addition of 10% sodium chloride to TF J (giving TF O) reduced the effectiveness of the LAS-containing member and improved the formulation which contained IA. In water of 135 ppm hardness, the sodium chloride improved the effectiveness of the member containing surfactant IA and was detrimental to the surfactant II composition. This was also true at 300 ppm hardness. Overall, while the use of sodium chloride in an acetate-NTA composition had no pronounced constant effect, it was not detrimental to the formulation.

In contrast to the soft water cleaning of D-II and E-LAS, which showed good detergency at 0.25% but dropped in efficiency at higher concentration, O-IA showed a steady increase in detergency with increasing concentration so that its cleaning ability approximated that of the "brand" at the highest concentration. On the other hand, the "O" Formulations were not as good as the "M" series in an overall comparison even though O-LAS and IA possessed the same high concentration cleaning ability in Chicago water.

The last formulation to be considered is "B" (Graphs 5-7) which contains 22% acetate in combination with 15% sodium sulfate. All members of this series tested rather poorly in soft water while the surfactant II-containing composition performed well in Chicago tap water. The hard water performance of B-IA and LAS were rather respectable while B-II was a poor performer at this hardness.

In general, the pH of the wash water which contained low concentrations of the phosphate-free formulations was somewhat deficient, being close to neutral instead of the desired 8-10.

SECTION V

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The concept of using potentially "self-chelating" surfactants in phosphate-free detergent formulations was fostered by Dr. Warner M. Linfield, Manager, Organic Chemistry Research Section, IIT Research Institute, while a number of additional formulation ideas were contributed by Dr. Karl A. Roseman, Research Chemist.

IITRI personnel who directly participated in this project include H. DeYoung, L. Hytry, M. Gould and C. Wetter of the Organic Chemistry Research Section as well as S. Miller and S. Vana of IITRI's Life Sciences Division.

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This project was designed, operated and administered by the IIT Research Institute; Dr. Warner M. Linfield was Project Director and Dr. Karl A. Roseman was Project Leader.

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SECTION VI

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SECTION VII

APPENDIX

Graph 1, page 32: Reference calibrations for surfactant-methylene blue complexes which were used in the presumptive biodegradability test.

Graphs 2-46, pages 33-77: Composite detergency curves for Formulations A through O as obtained using the U. S. Testing Co. standard soiled cotton cloth.

Synthetic Procedures and Analyses for the Surfactants

Surfactant IA: Sodium dodecylbenzenesulfonamidoethyl sulfate ($C_{12}H_{25}C_6H_4SO_2NHCH_2CH_2OSO_3Na$)

Surfactant IB1: Sodium dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}-C_6H_4-SO_2NHCH_2CH_2SO_3Na$)

Surfactant IB2: Sodium N-methyl-dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}C_6H_4SO_2N(CH_3)CH_2CH_2SO_3Na$)

Surfactant II: Methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)propionate ($C_{12}H_{25}C_6H_4COCH(SO_3Na)CH_2CO_2CH_3$)

Surfactant IIIA: Sodium dodecylaminoethanesulfonate ($C_{12}H_{25}NHCH_2CH_2SO_3Na$)

Surfactant IIIB: Sodium N-hydroxyethyl-2-dodecylaminoethanesulfonate ($C_{12}H_{25}N(CH_2CH_2OH)CH_2CH_2SO_3Na$)

Surfactant IVA: Dodecyl 3-(sodium levulinate) sulfone ($C_{12}H_{25}SO_2CH(COCH_3)CH_2CO_2Na$)

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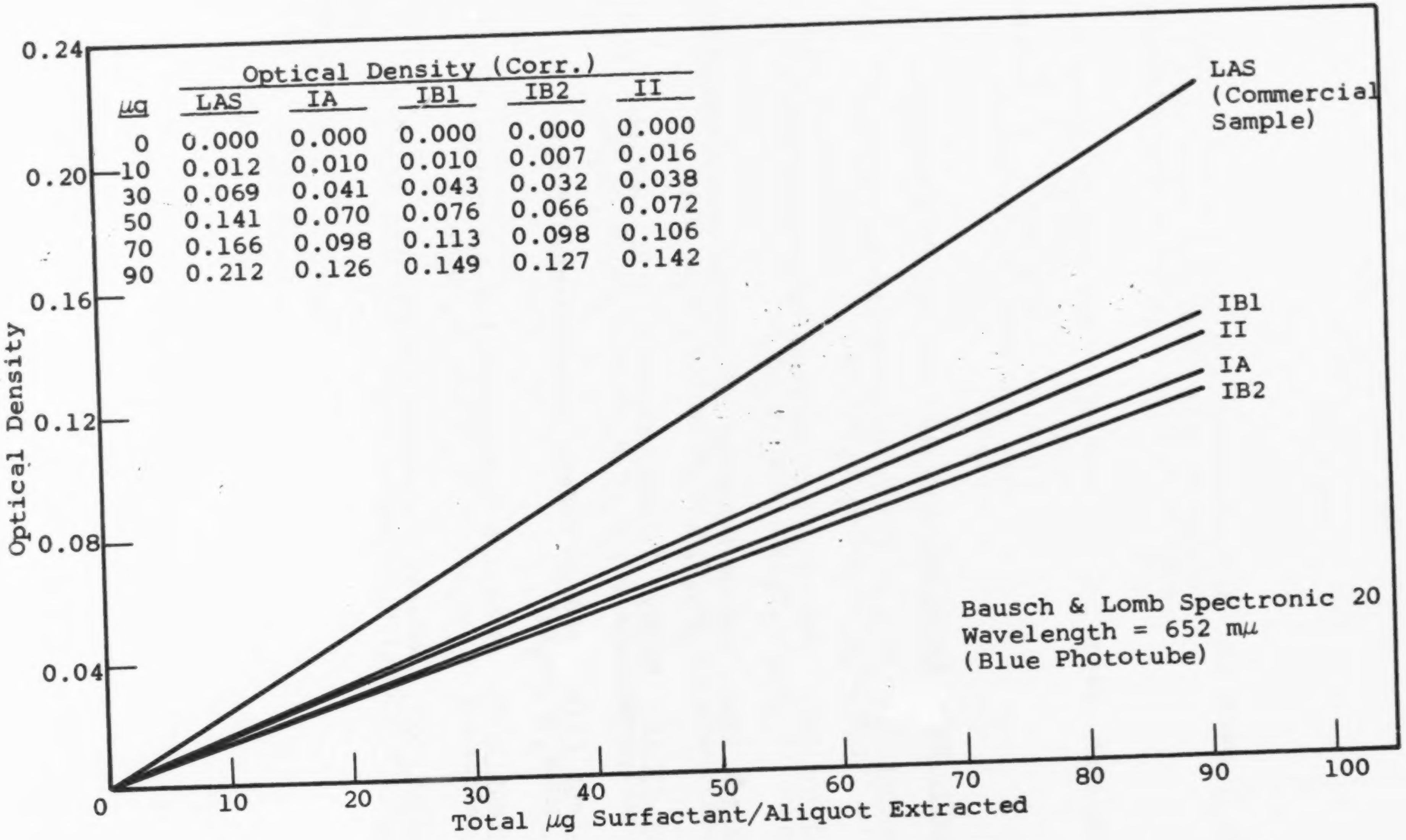
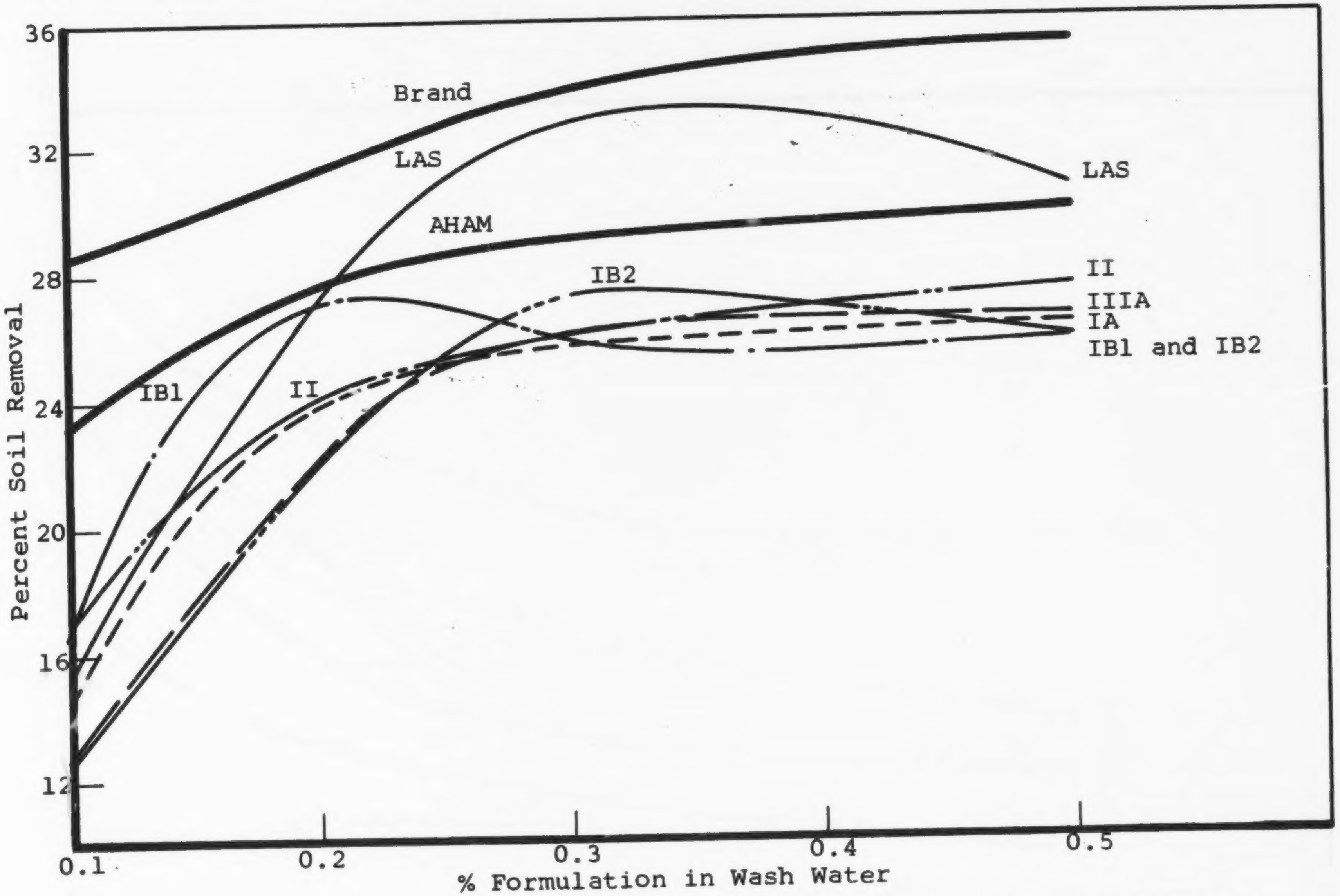
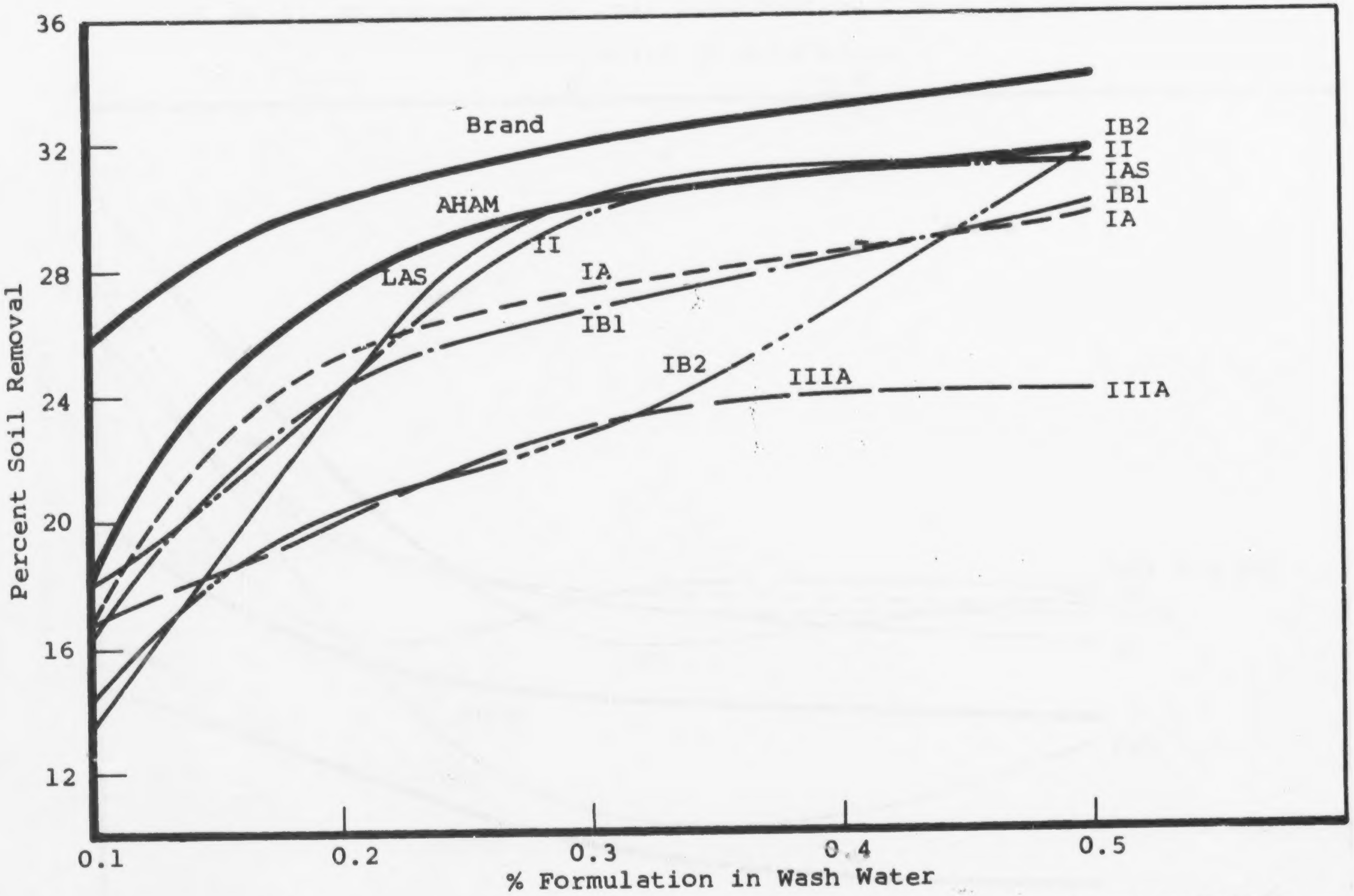


μg	Optical Density (Corr.)				
	LAS	IA	IB1	IB2	II
0	0.000	0.000	0.000	0.000	0.000
10	0.012	0.010	0.010	0.007	0.016
30	0.069	0.041	0.043	0.032	0.038
50	0.141	0.070	0.076	0.066	0.072
70	0.166	0.098	0.113	0.098	0.106
90	0.212	0.126	0.149	0.127	0.142

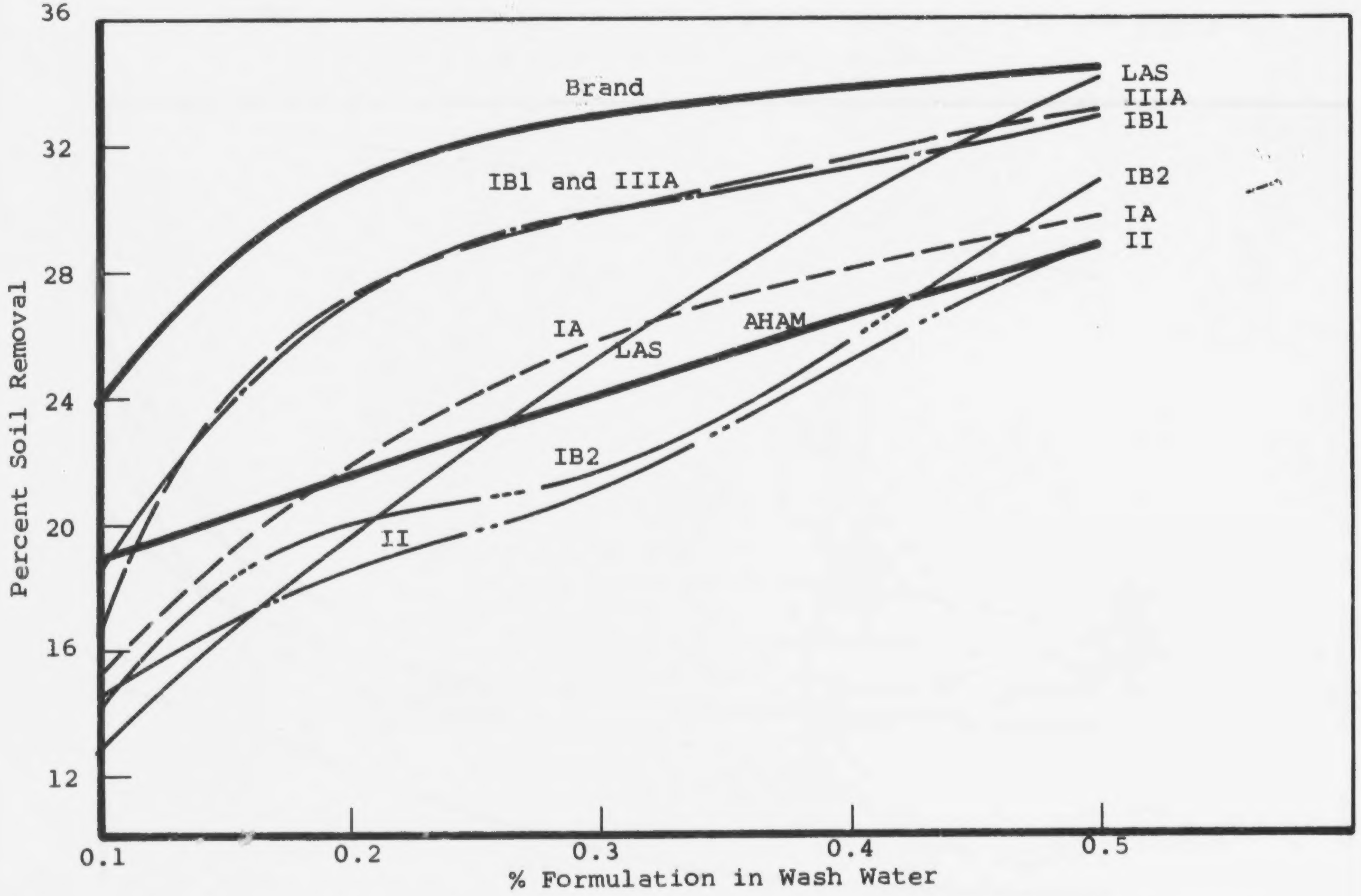
Graph 1. REFERENCE CALIBRATIONS FOR SURFACTANT-METHYLENE BLUE COMPLEX



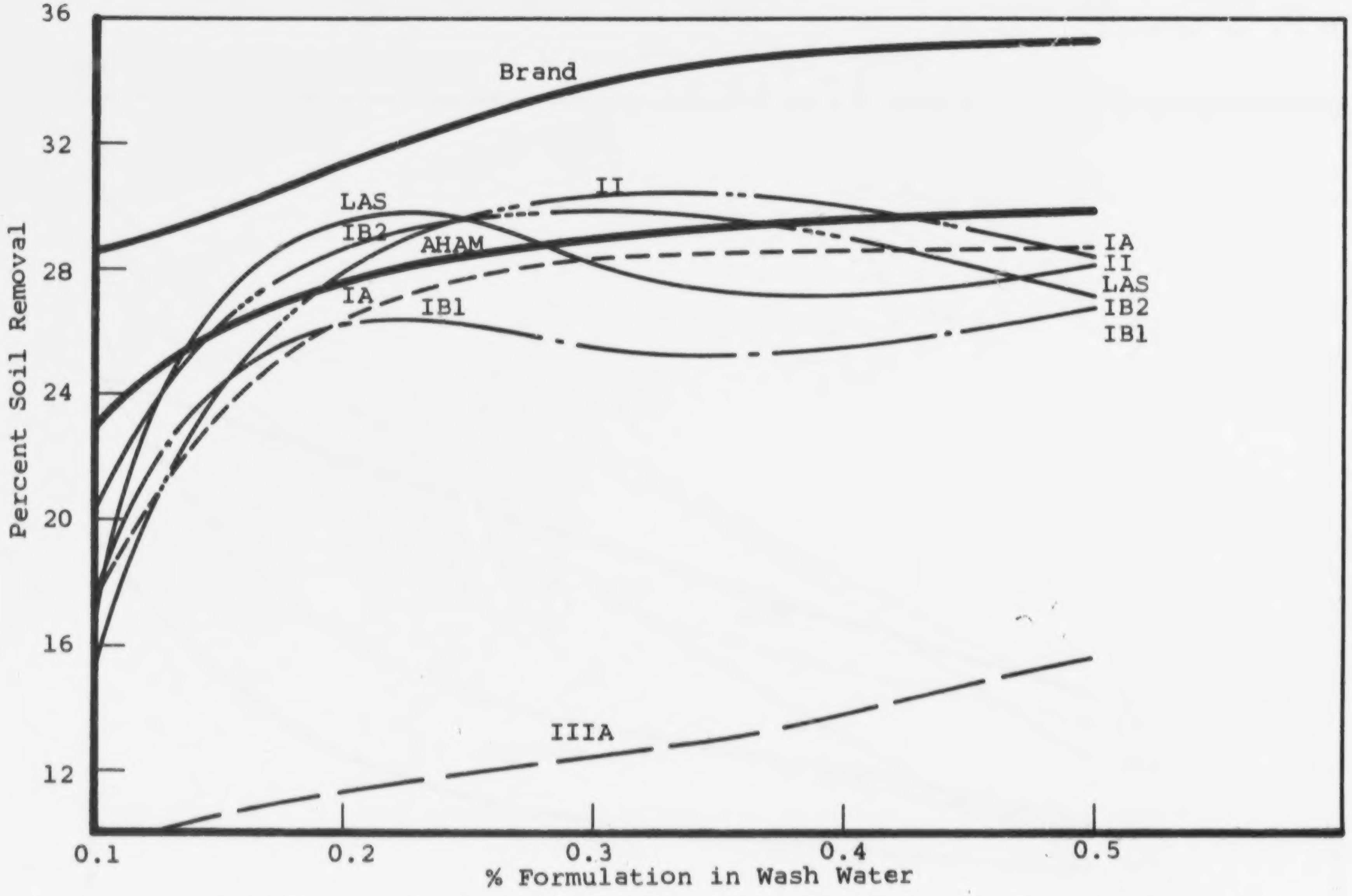
Graph 2. DETERGENCIES OF TEST FORMULATIONS "A" AT 50 PPM HARDNESS



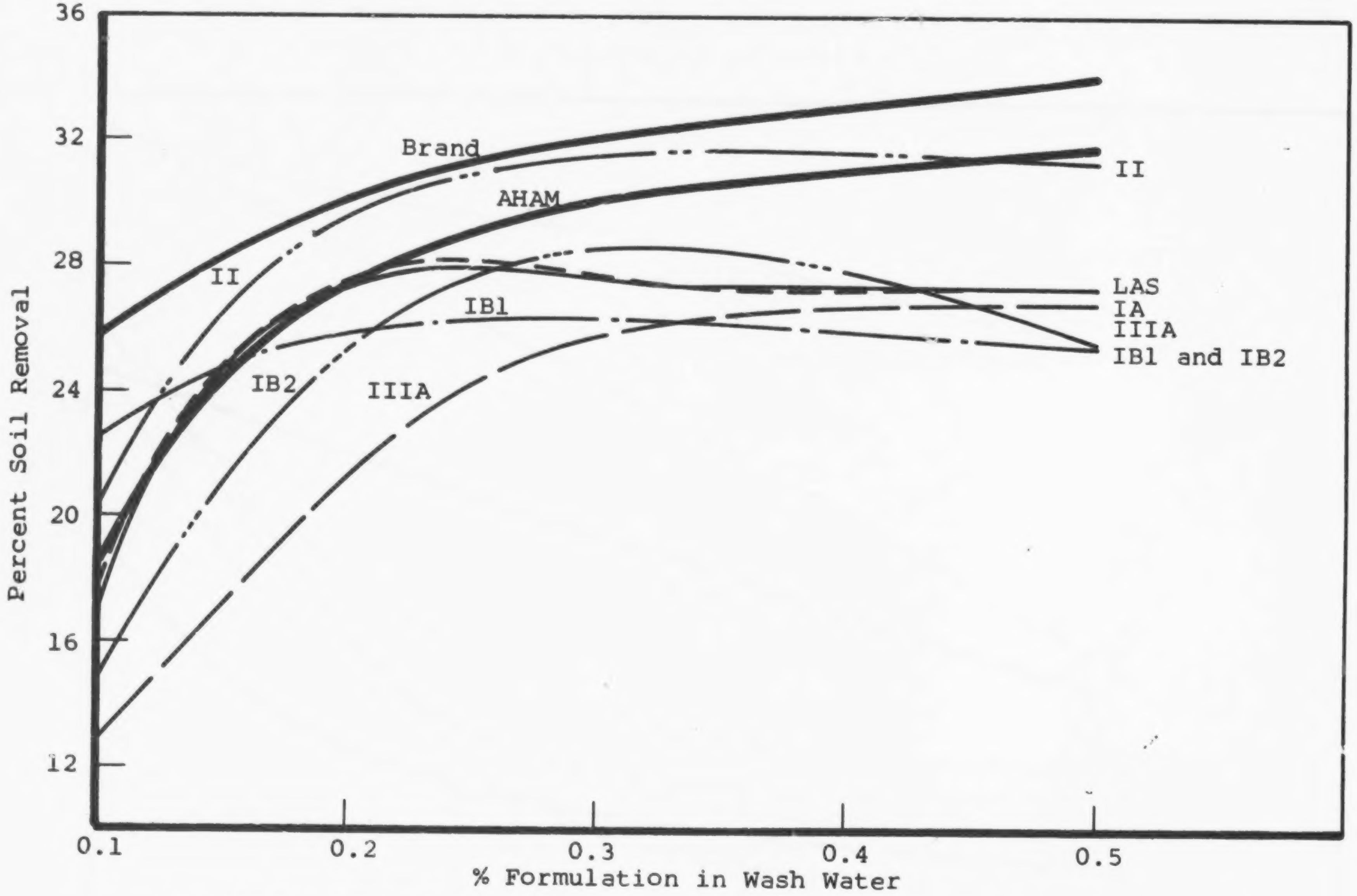
Graph 3. DETERGENCIES OF TEST FORMULATIONS "A" AT 135 PPM HARDNESS



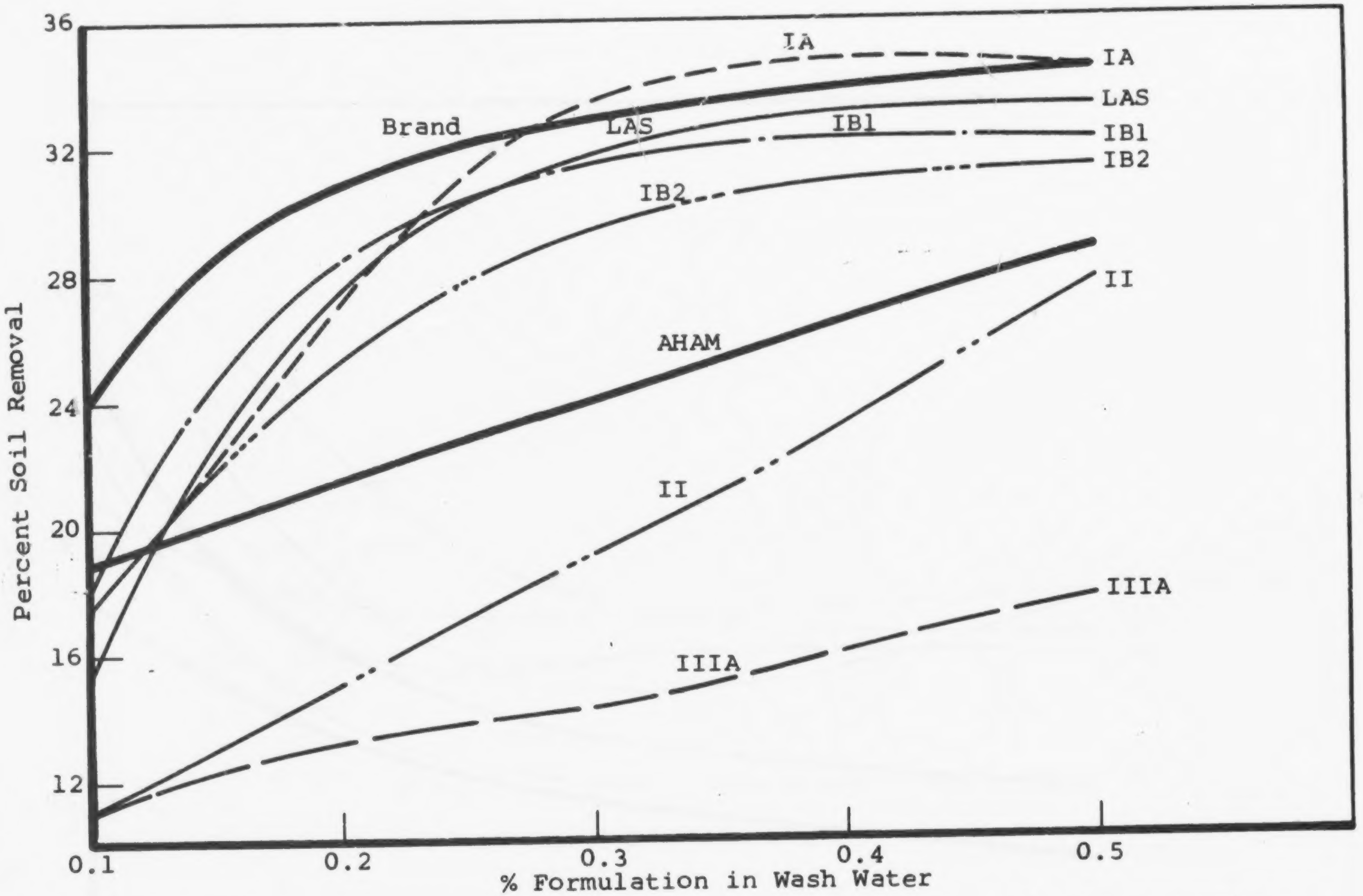
Graph 4. DETERGENCIES OF TEST FORMULATIONS "A" AT 300 PPM HARDNESS



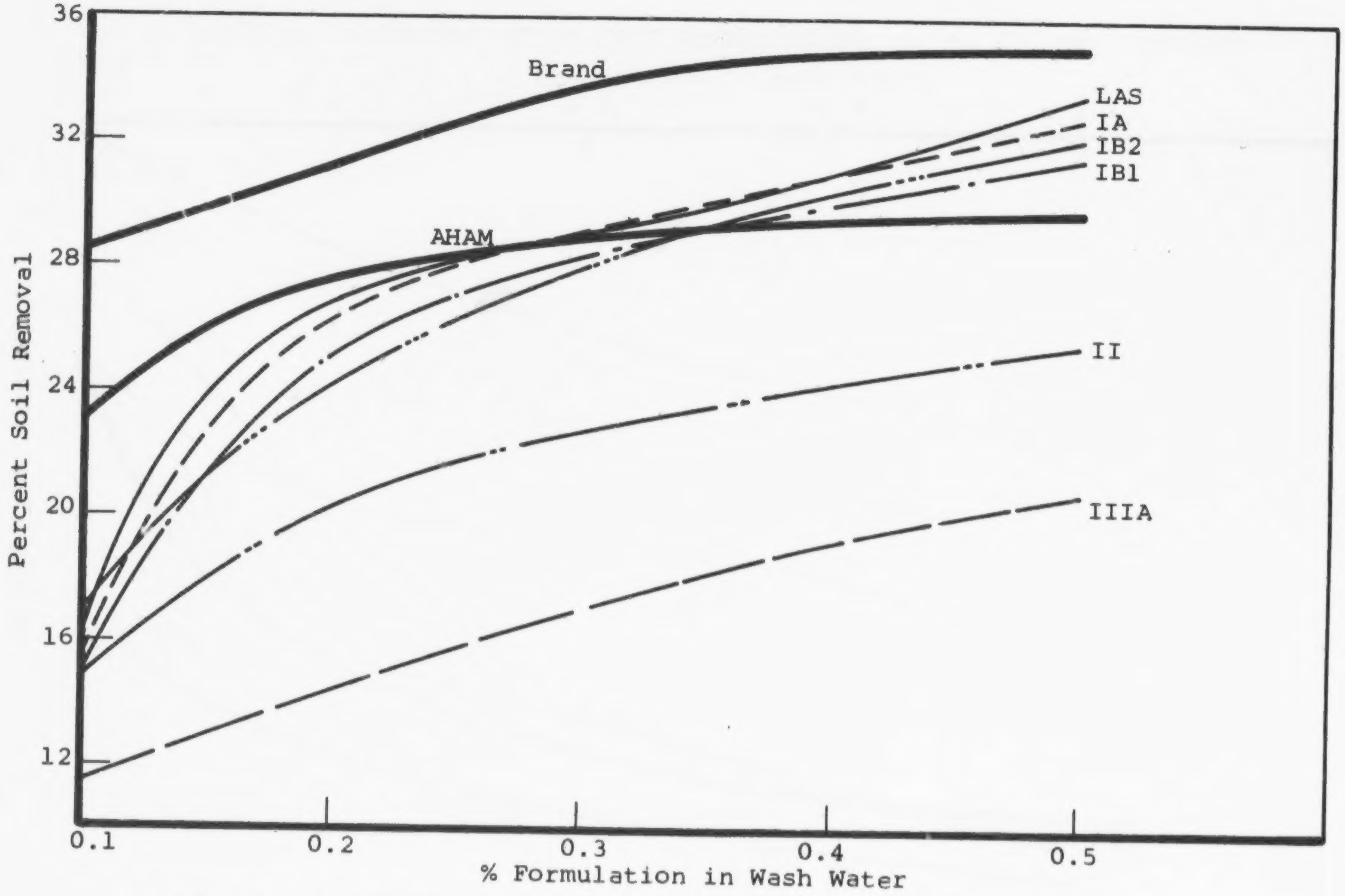
Graph 5. DETERGENCIES OF TEST FORMULATIONS "B" AT 50 PPM HARDNESS



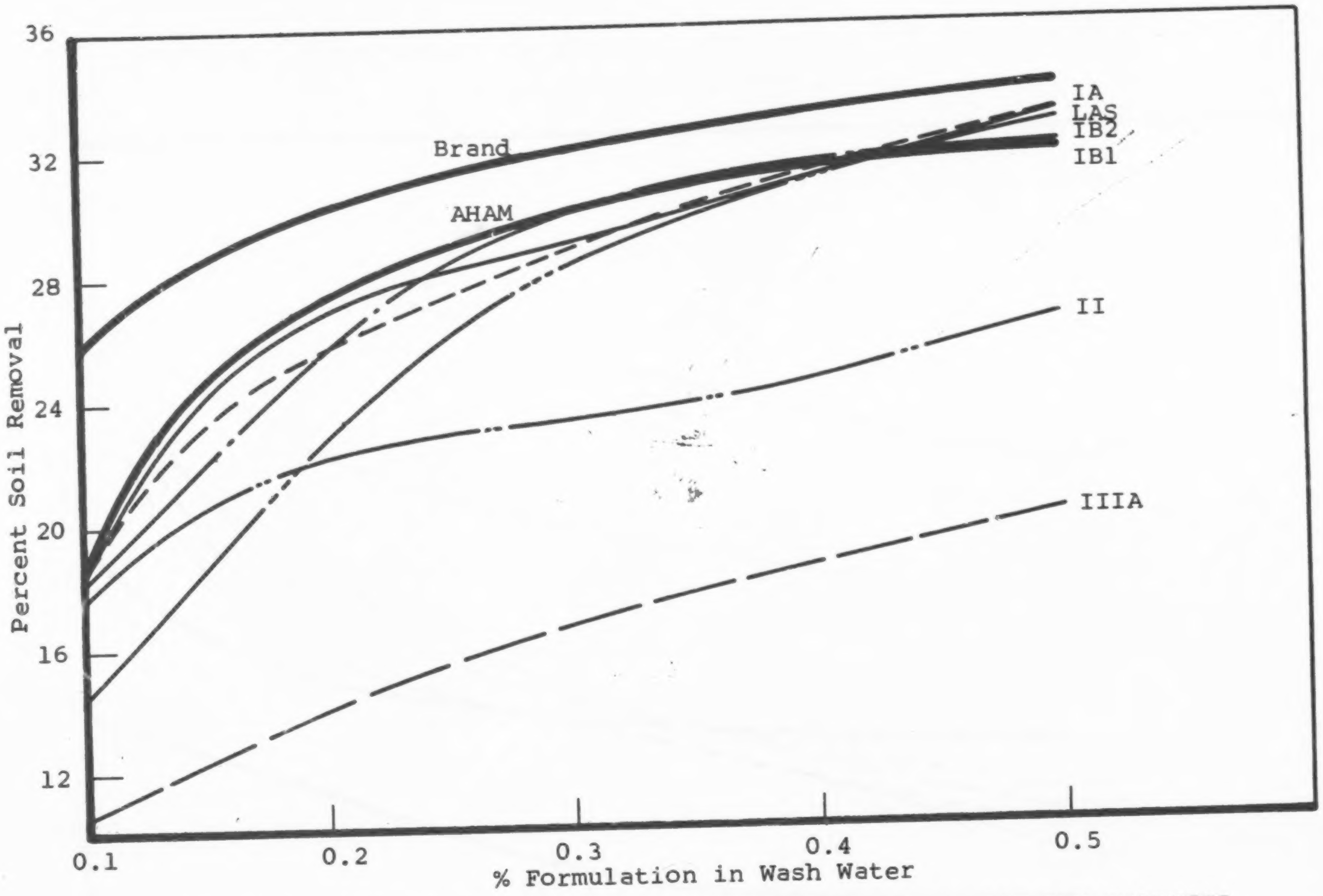
Graph 6. DETERGENCIES OF TEST FORMULATIONS "B" AT 135 PPM HARDNESS



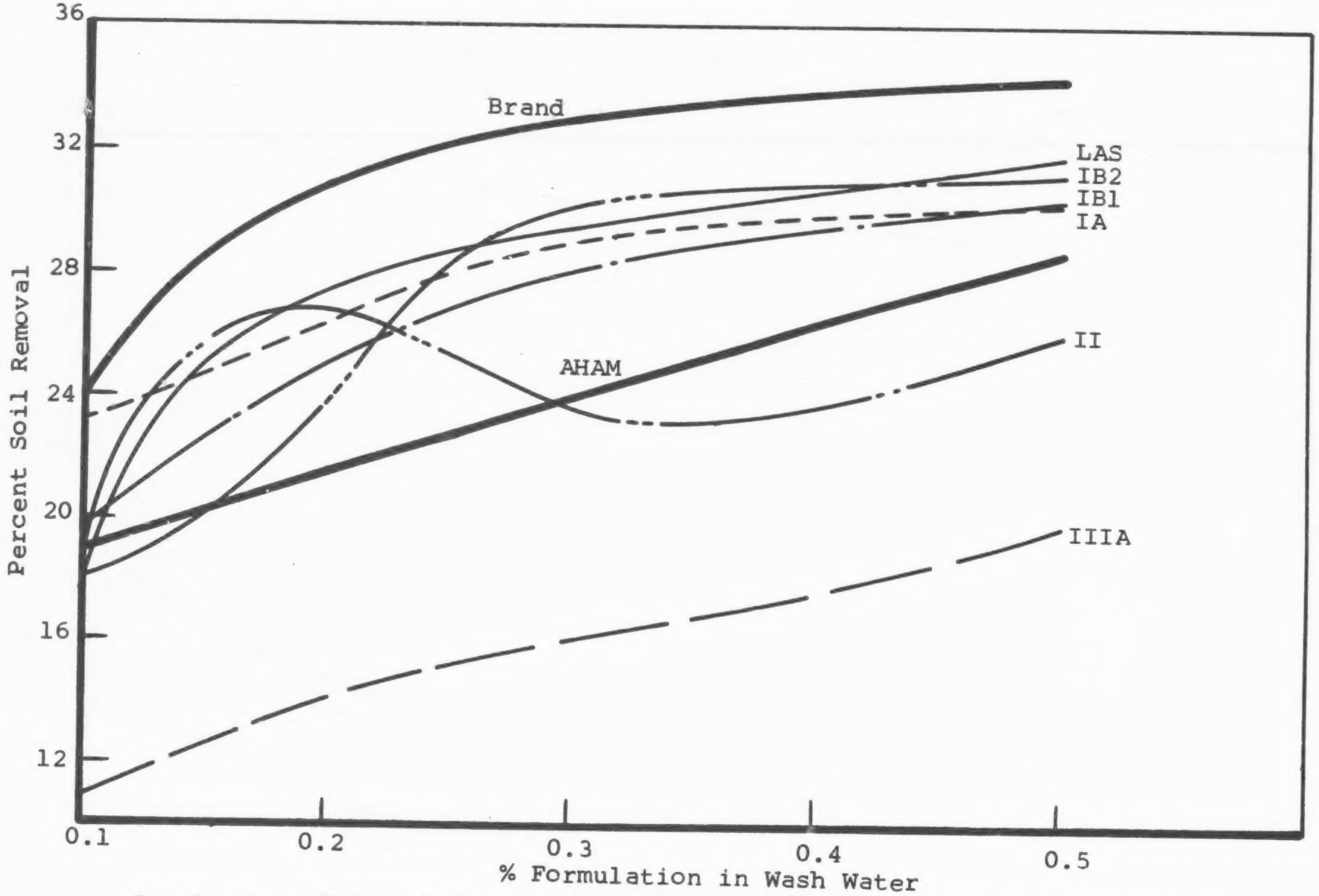
Graph 7. DETERGENCIES OF TEST FORMULATIONS "B" AT 300 PPM HARDNESS



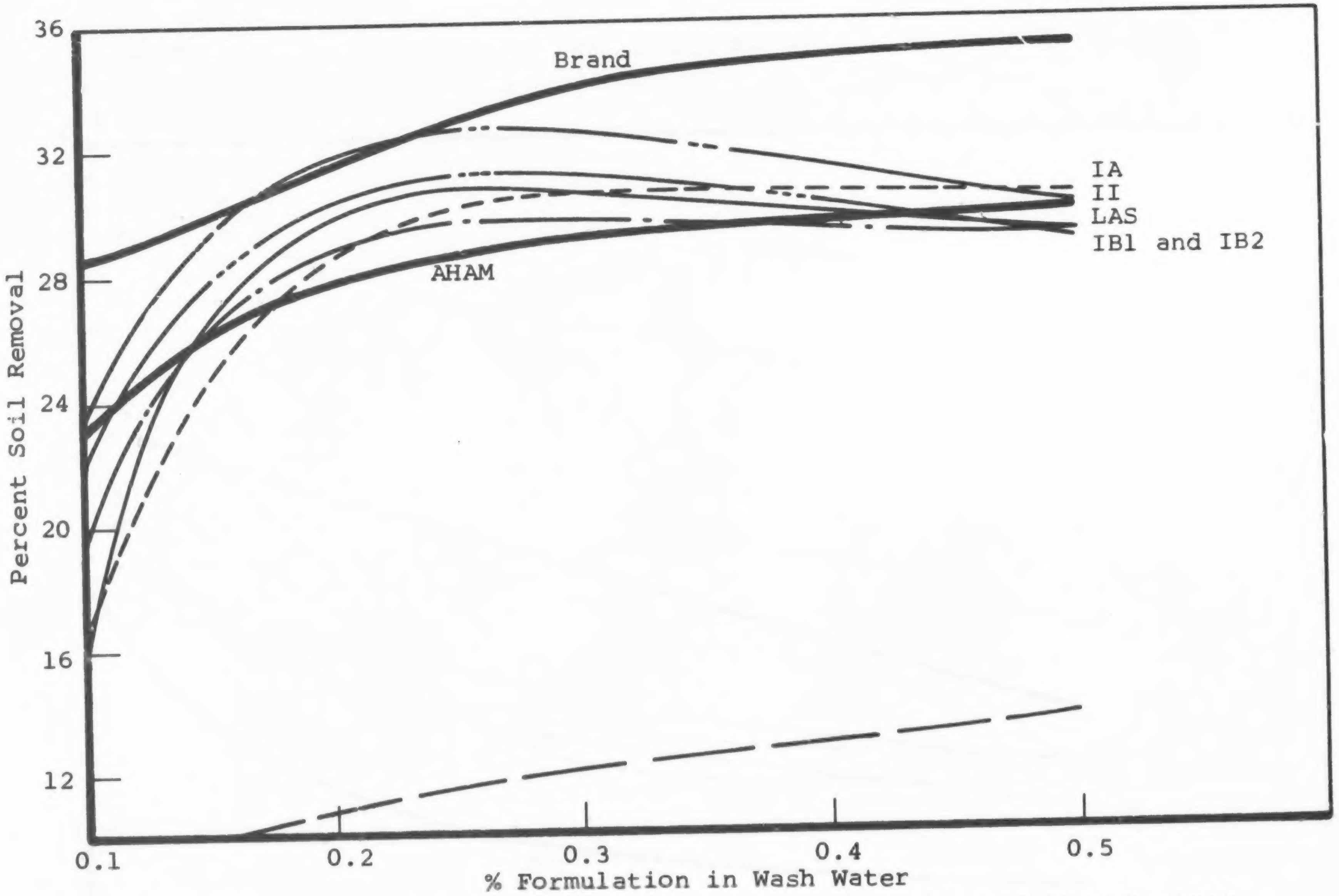
Graph 8. DETERGENCIES OF TEST FORMULATIONS "C" AT 50 PPM HARDNESS



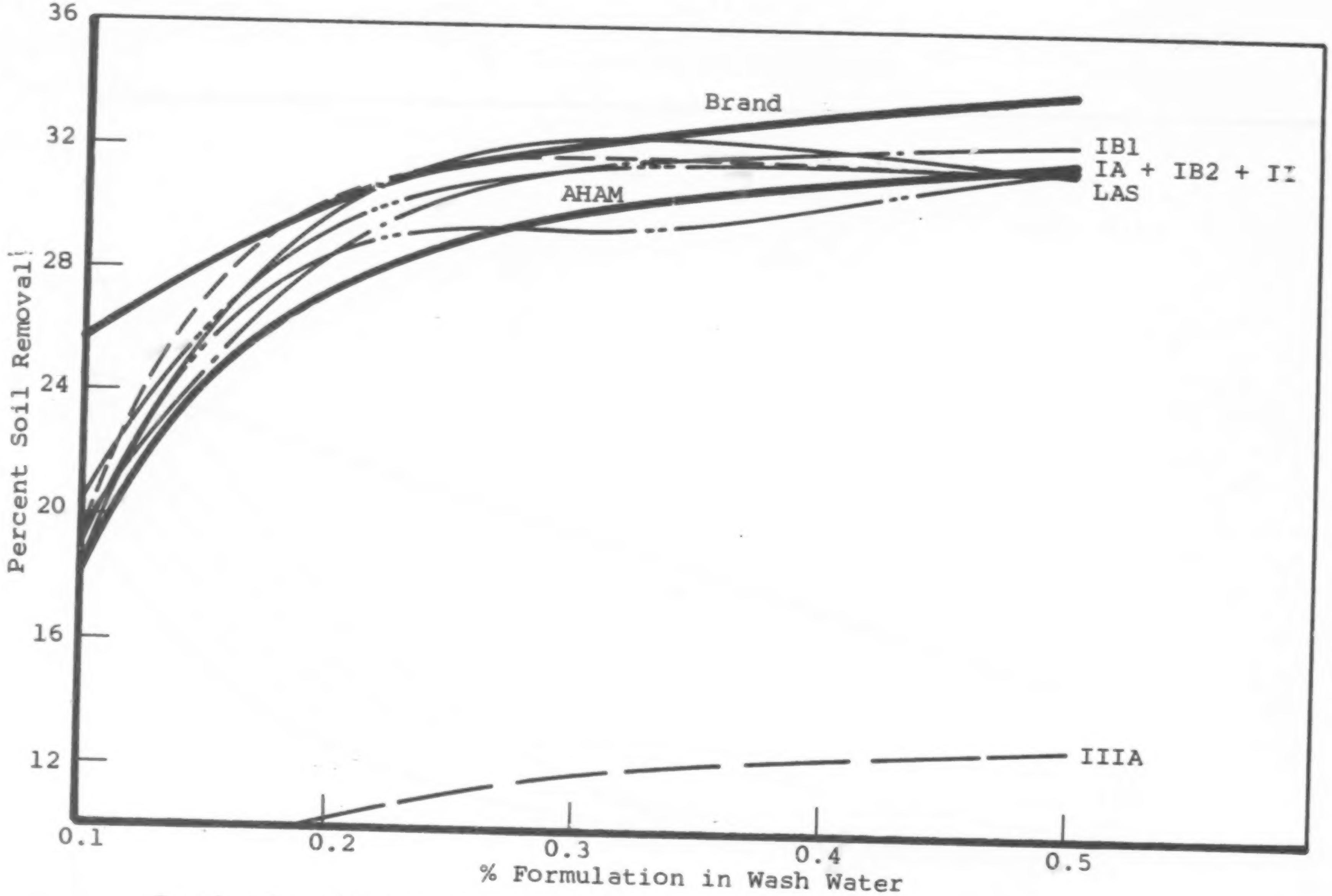
Graph 9. DETERGENCIES OF TEST FORMULATIONS "C" AT 135 PPM HARDNESS



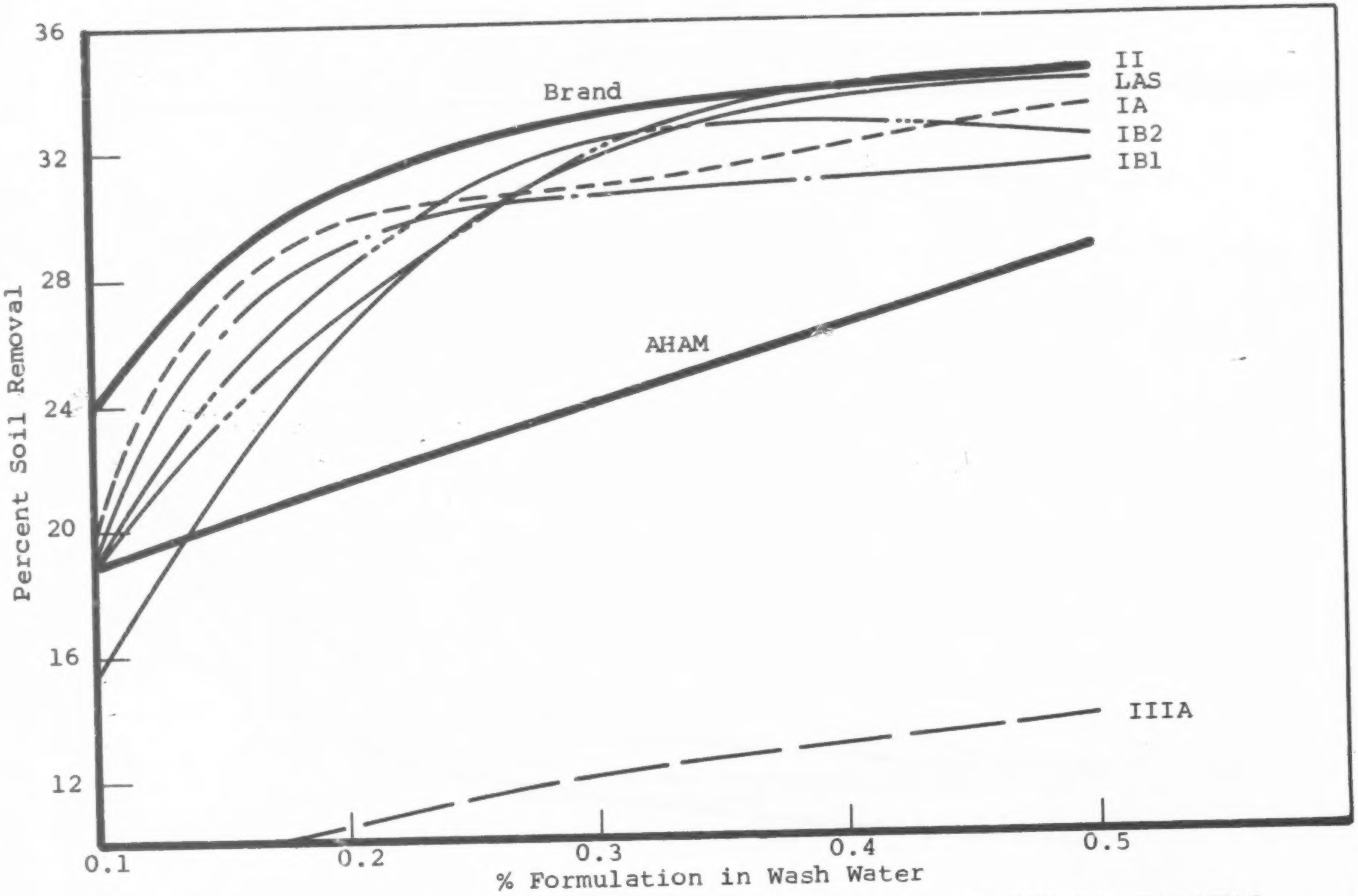
Graph 10. DETERGENCIES OF TEST FORMULATIONS "C" AT 300 PPM HARDNESS



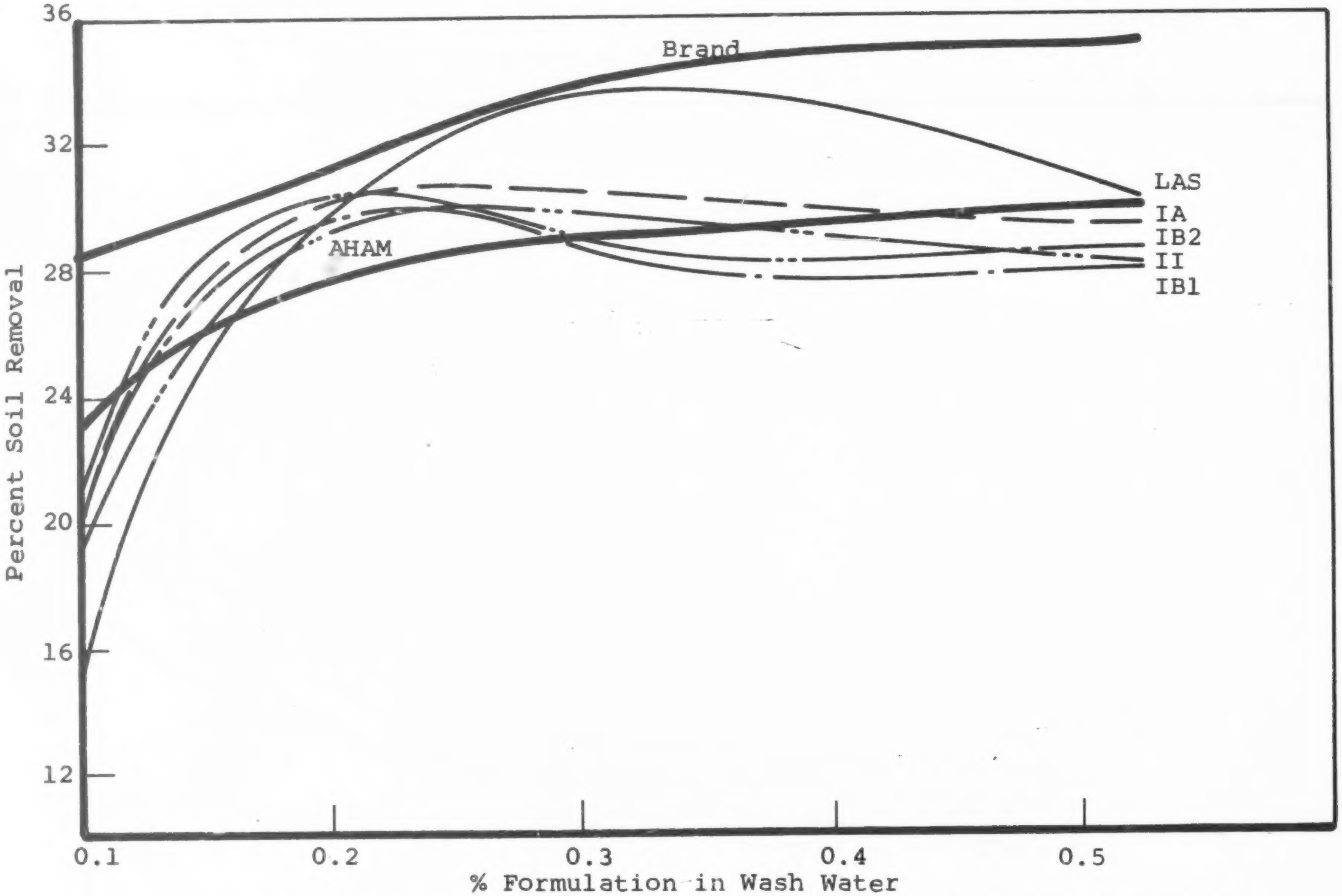
Graph 11. DETERGENCIES OF TEST FORMULATIONS "D" AT 50 PPM HARDNESS



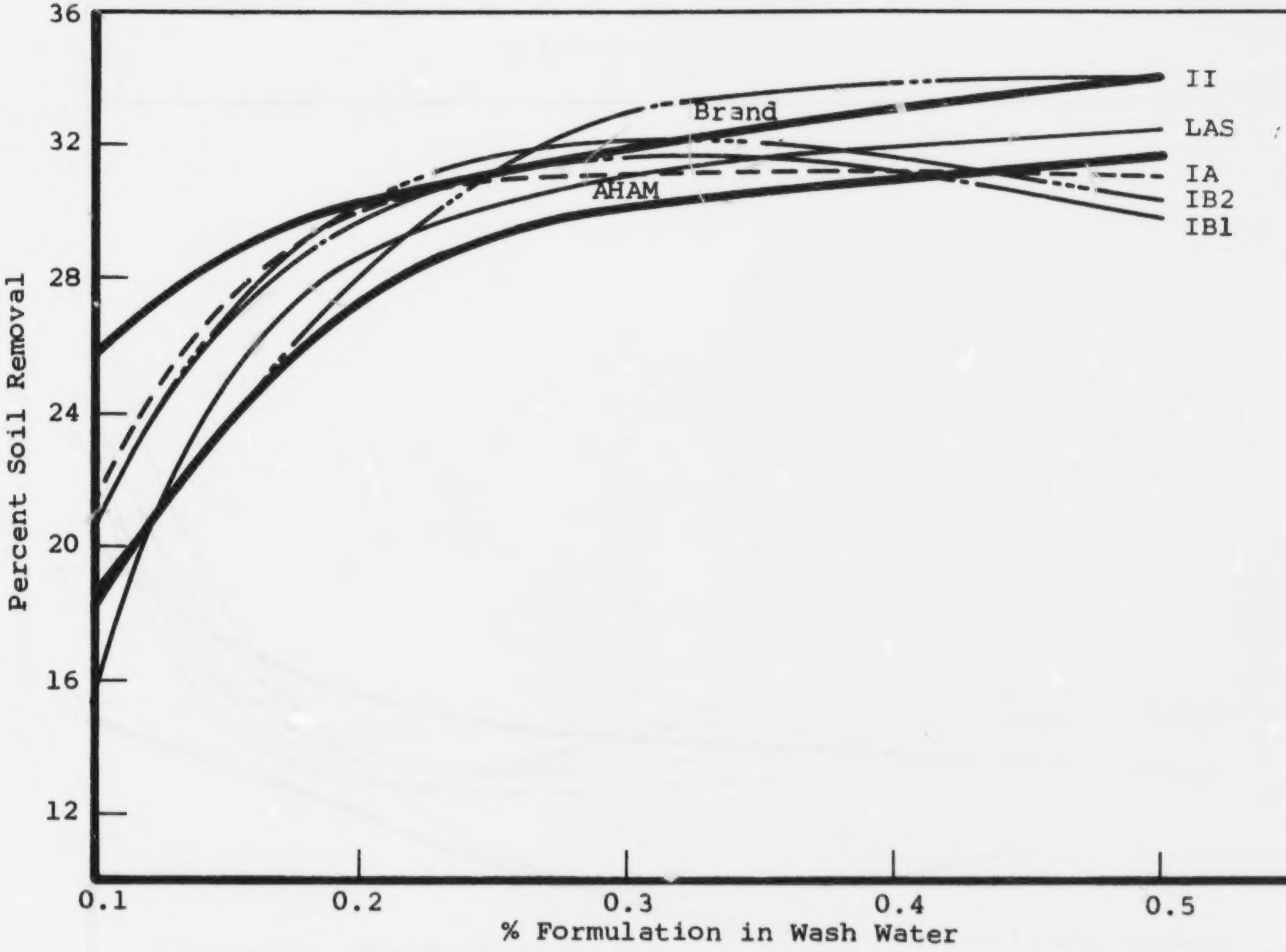
Graph 12. DETERGENCIES OF TEST FORMULATIONS "D" AT 135 PPM HARDNESS



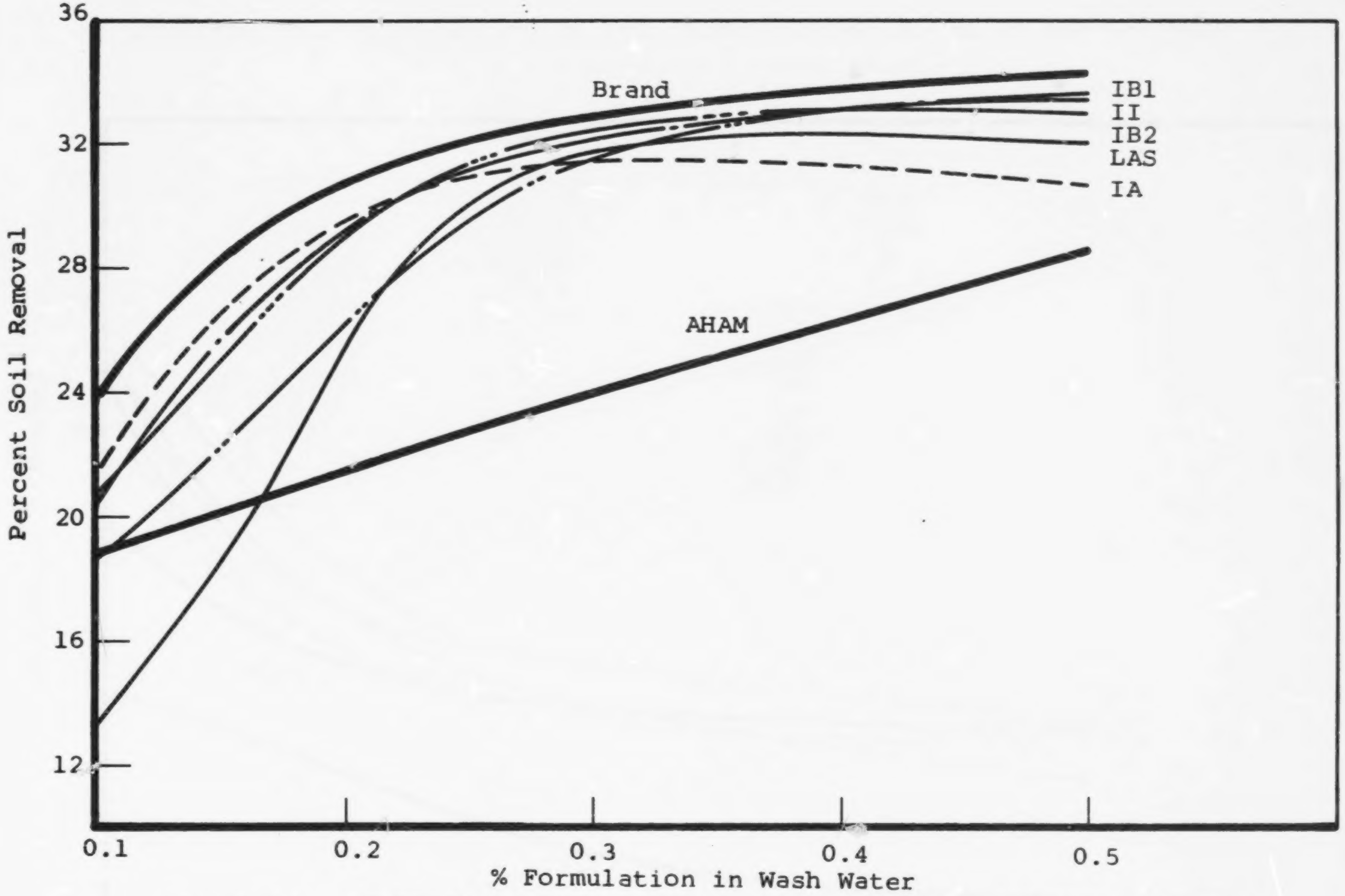
Graph 13. DETERGENCIES OF TEST FORMULATIONS "D" AT 300 PPM HARDNESS



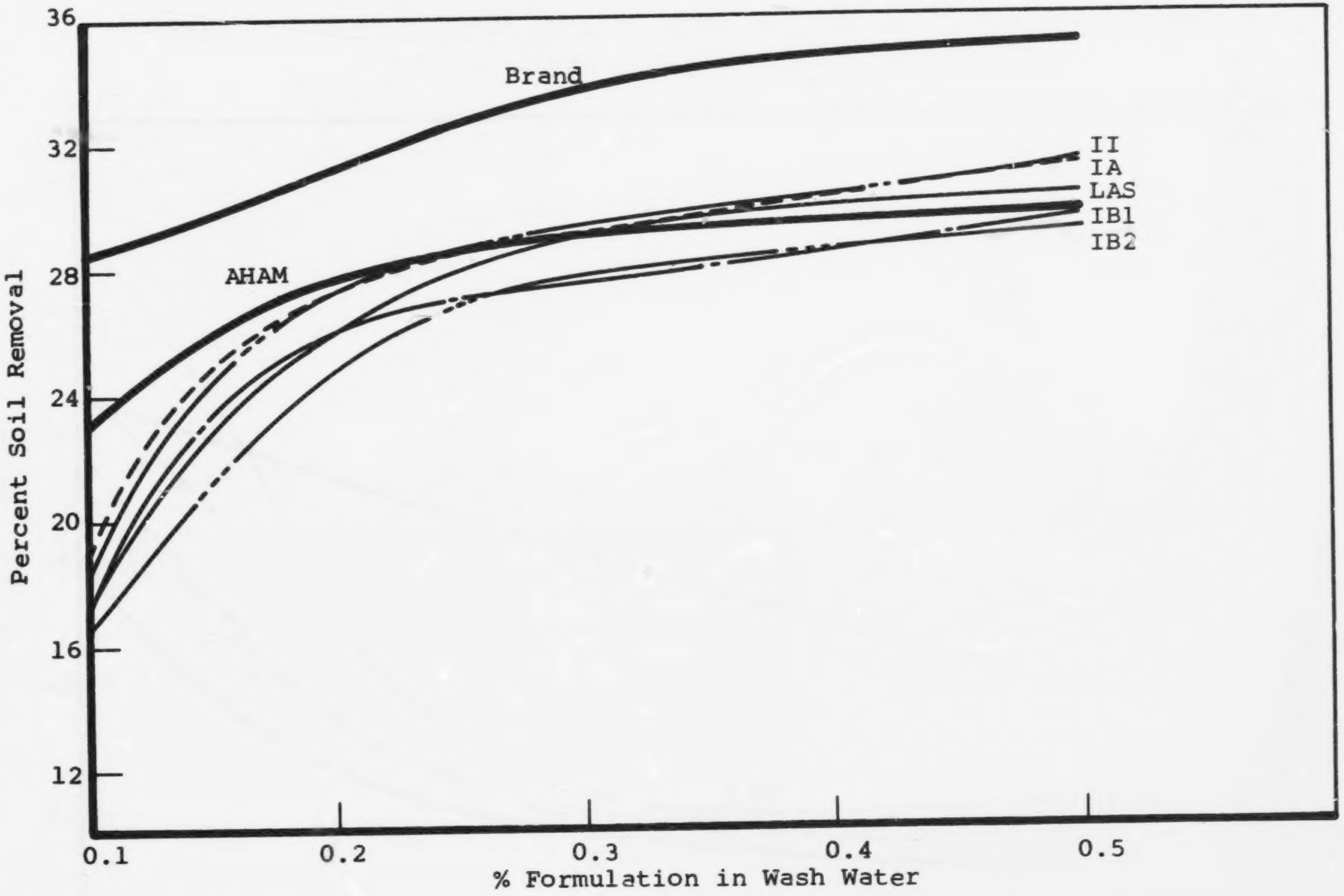
Graph 14. DETERGENCIES OF TEST FORMULATIONS "E" AT 50 PPM HARDNESS



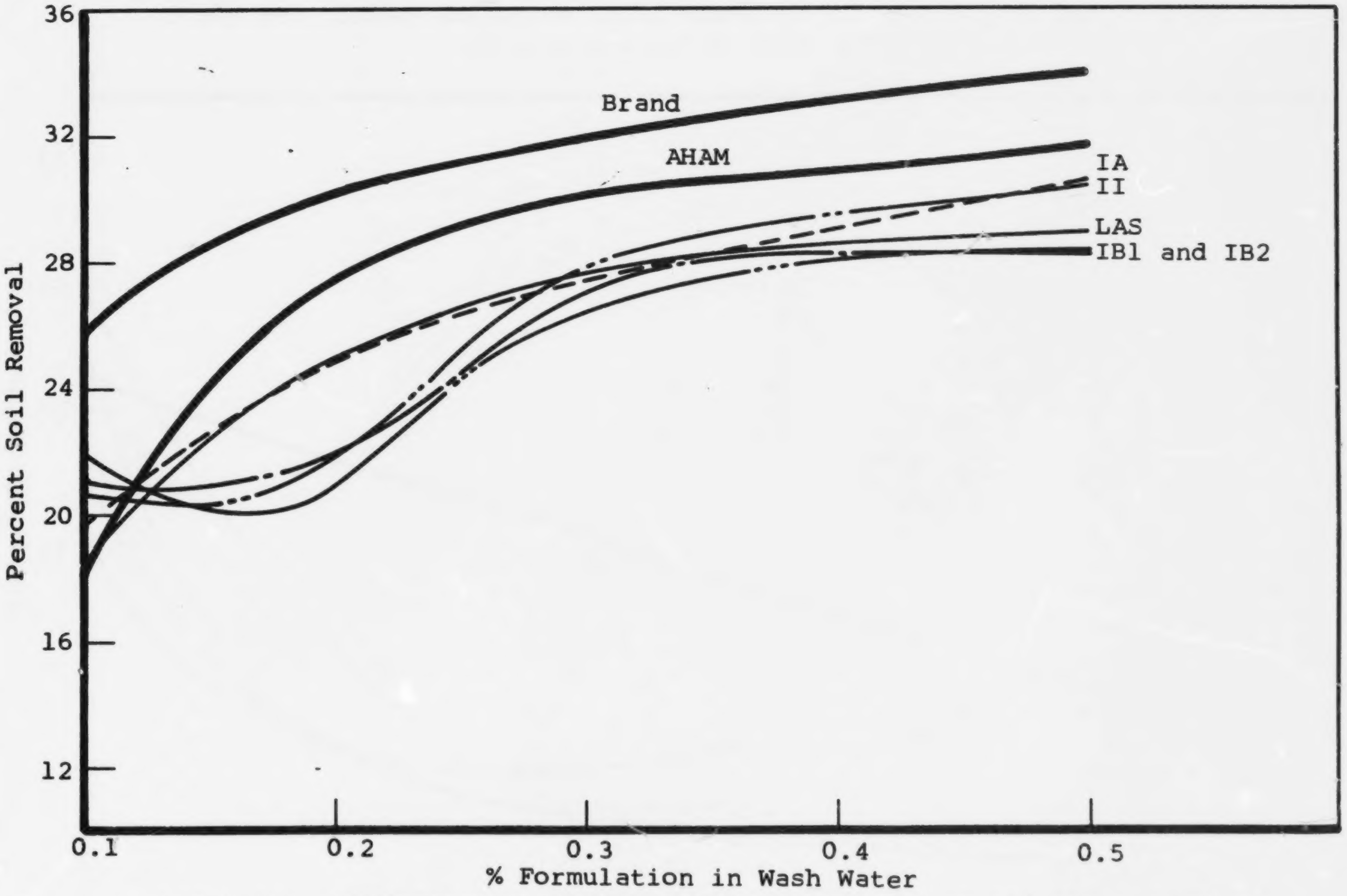
Graph 15. DETERGENCIES OF TEST FORMULATIONS "E" AT 135 PPM HARDNESS



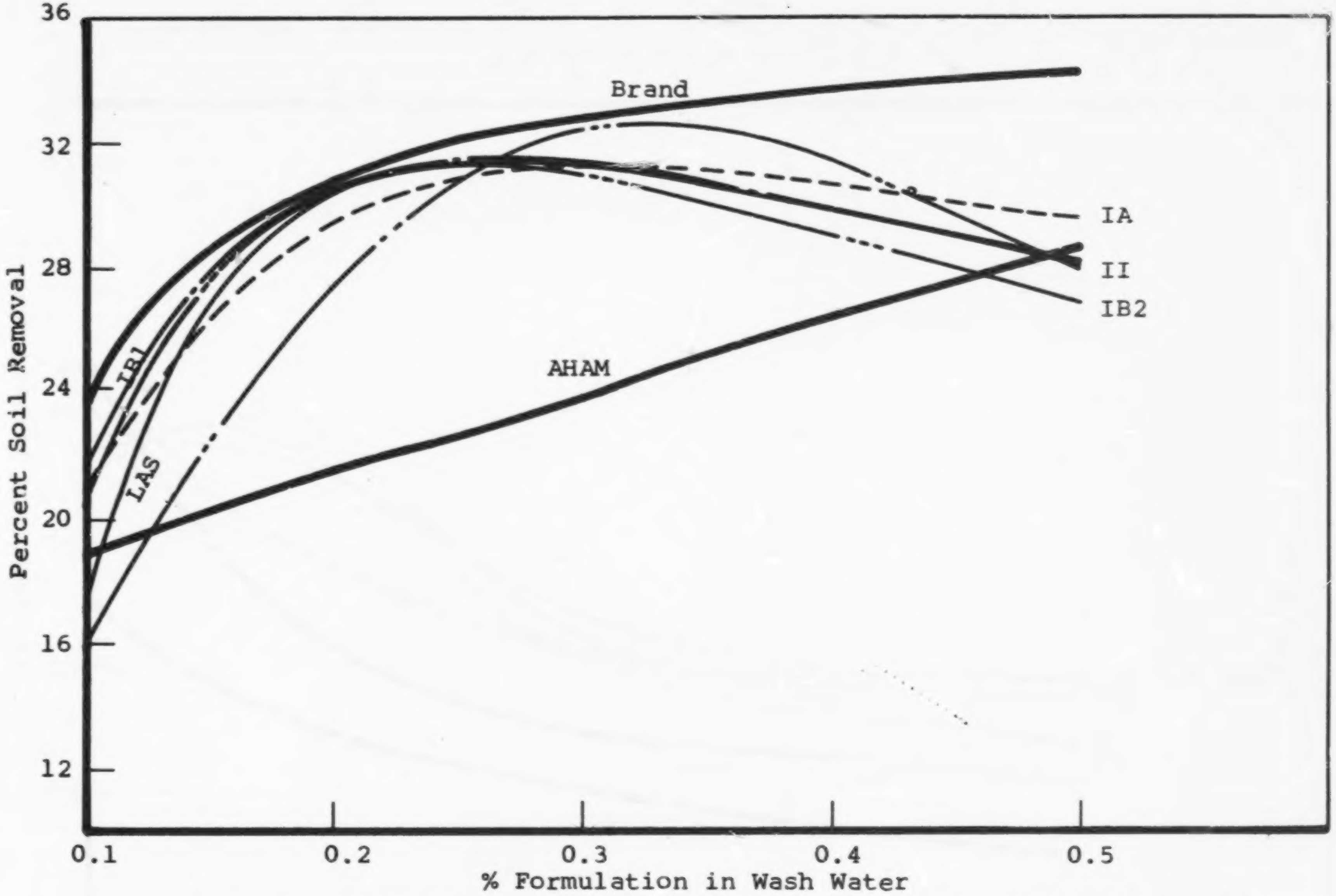
Graph 16. DETERGENCIES OF TEST FORMULATIONS "E" AT 300 PPM HARDNESS



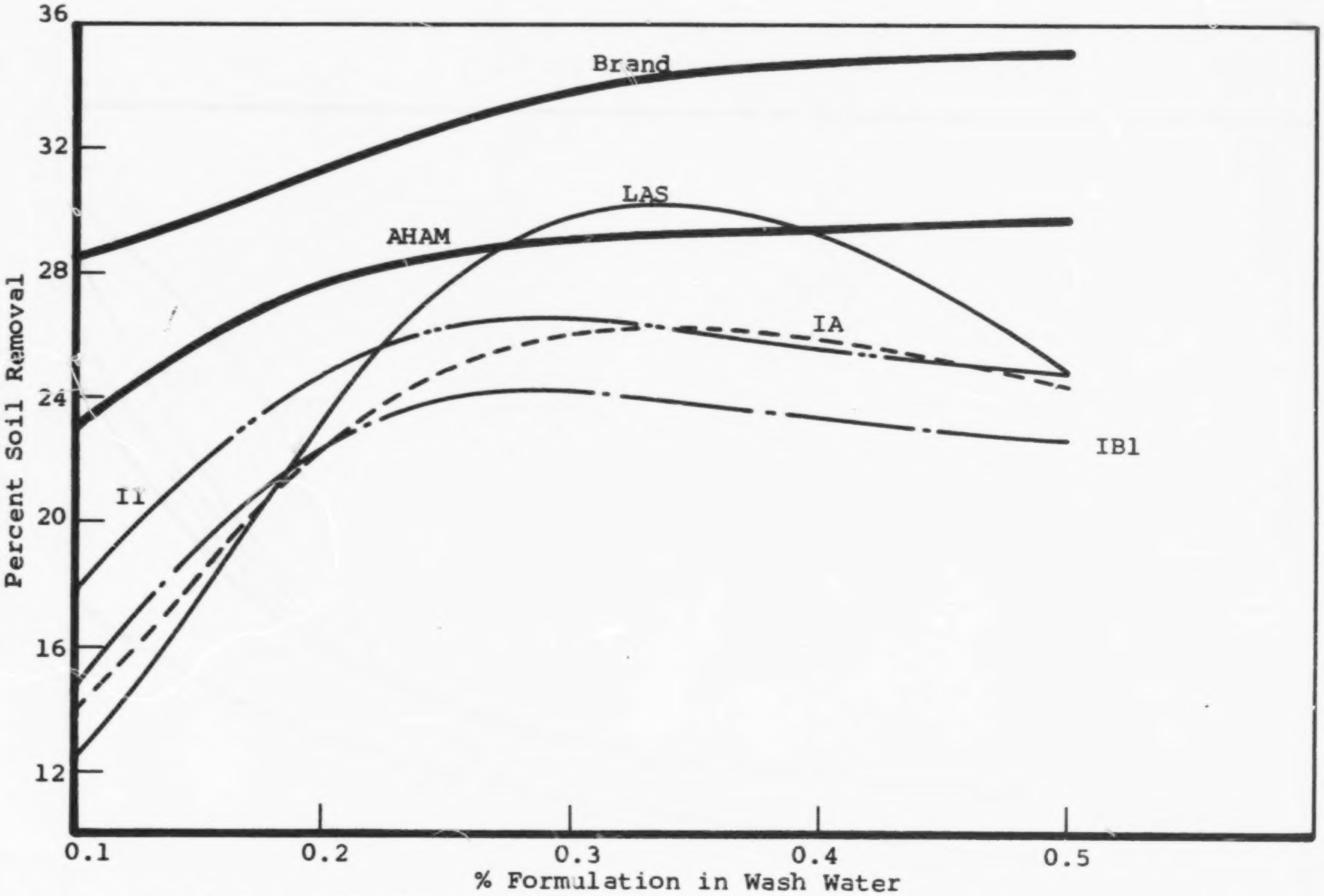
Graph 17. DETERGENCIES OF TEST FORMULATIONS "F" AT 50 PPM HARDNESS



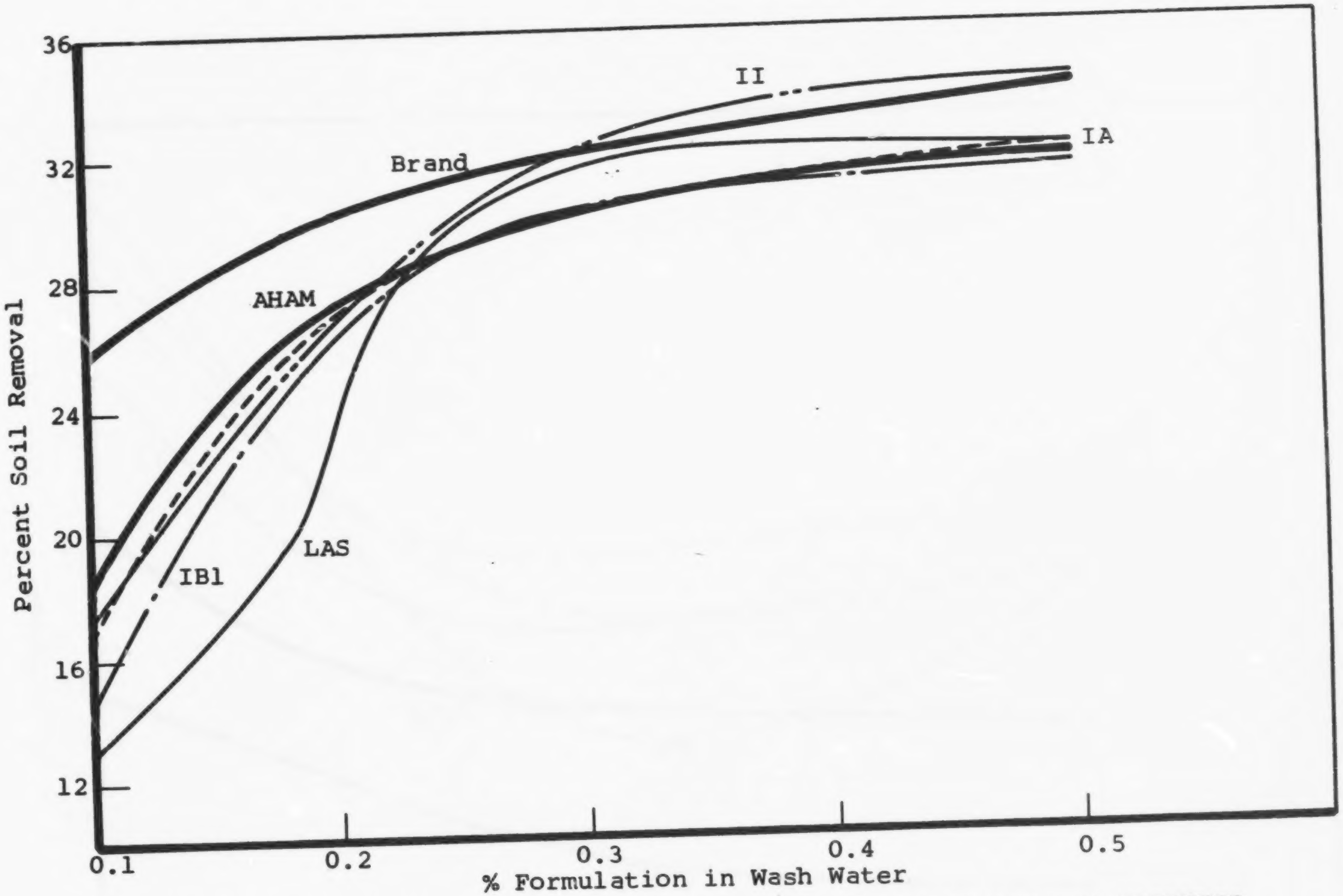
Graph 18. DETERGENCIES OF TEST FORMULATIONS "F" AT 135 PPM HARDNESS



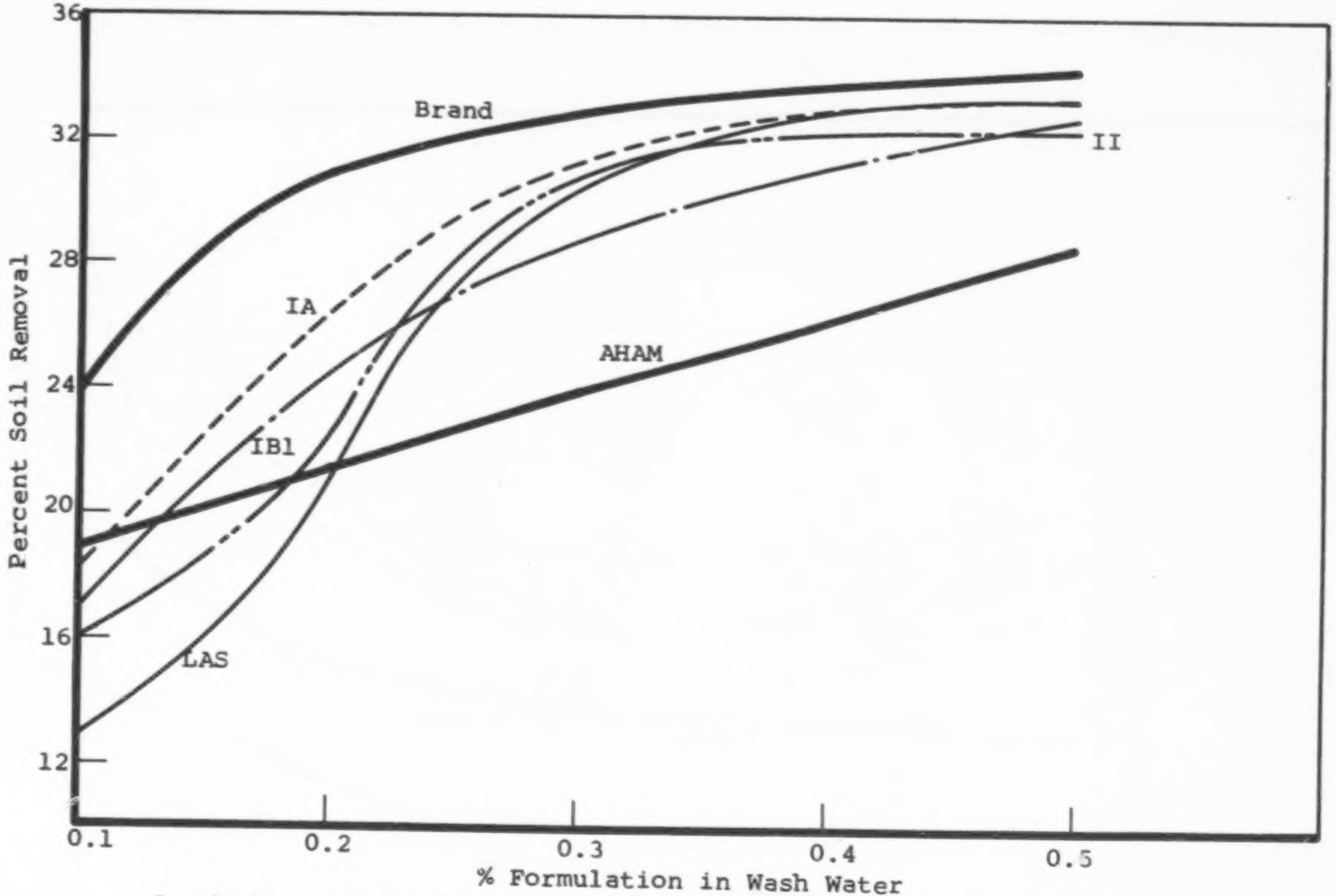
Graph 19. DETERGENCIES OF TEST FORMULATIONS "F" AT 300 PPM HARDNESS



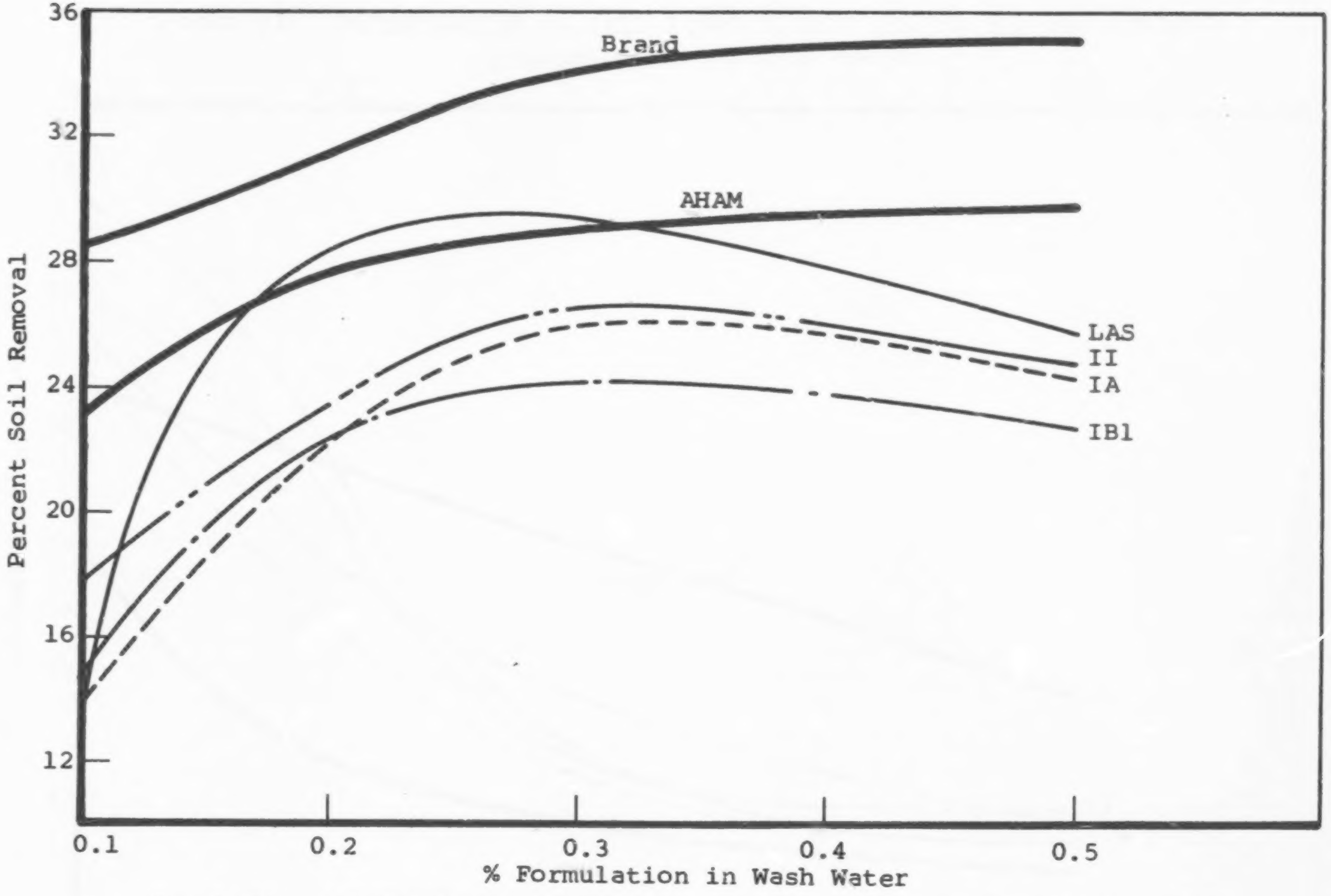
Graph 20. DETERGENCIES OF TEST FORMULATIONS "G" AT 50 PPM HARDNESS



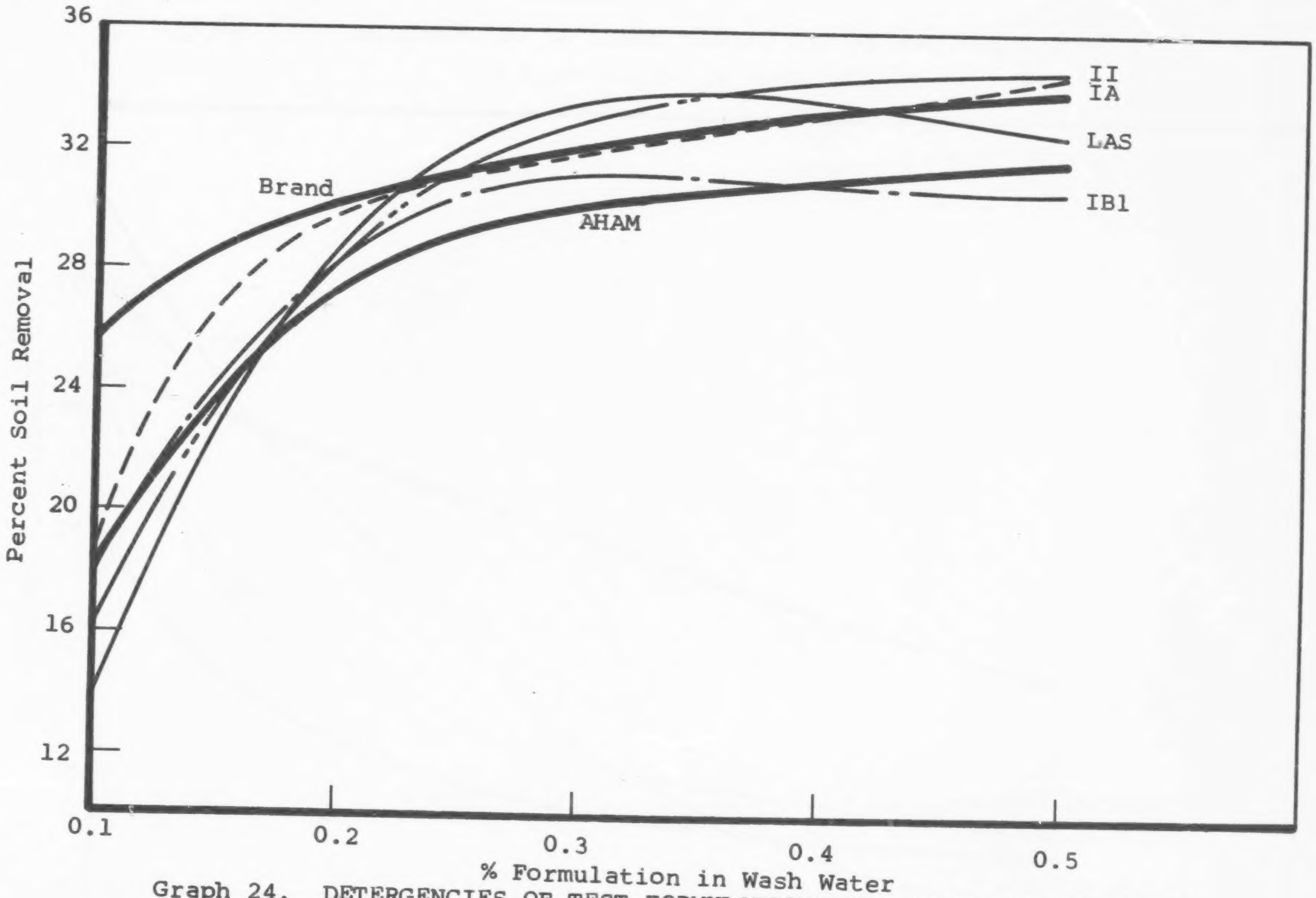
Graph 21. DETERGENCIES OF TEST FORMULATIONS "G" AT 135 PPM HARDNESS



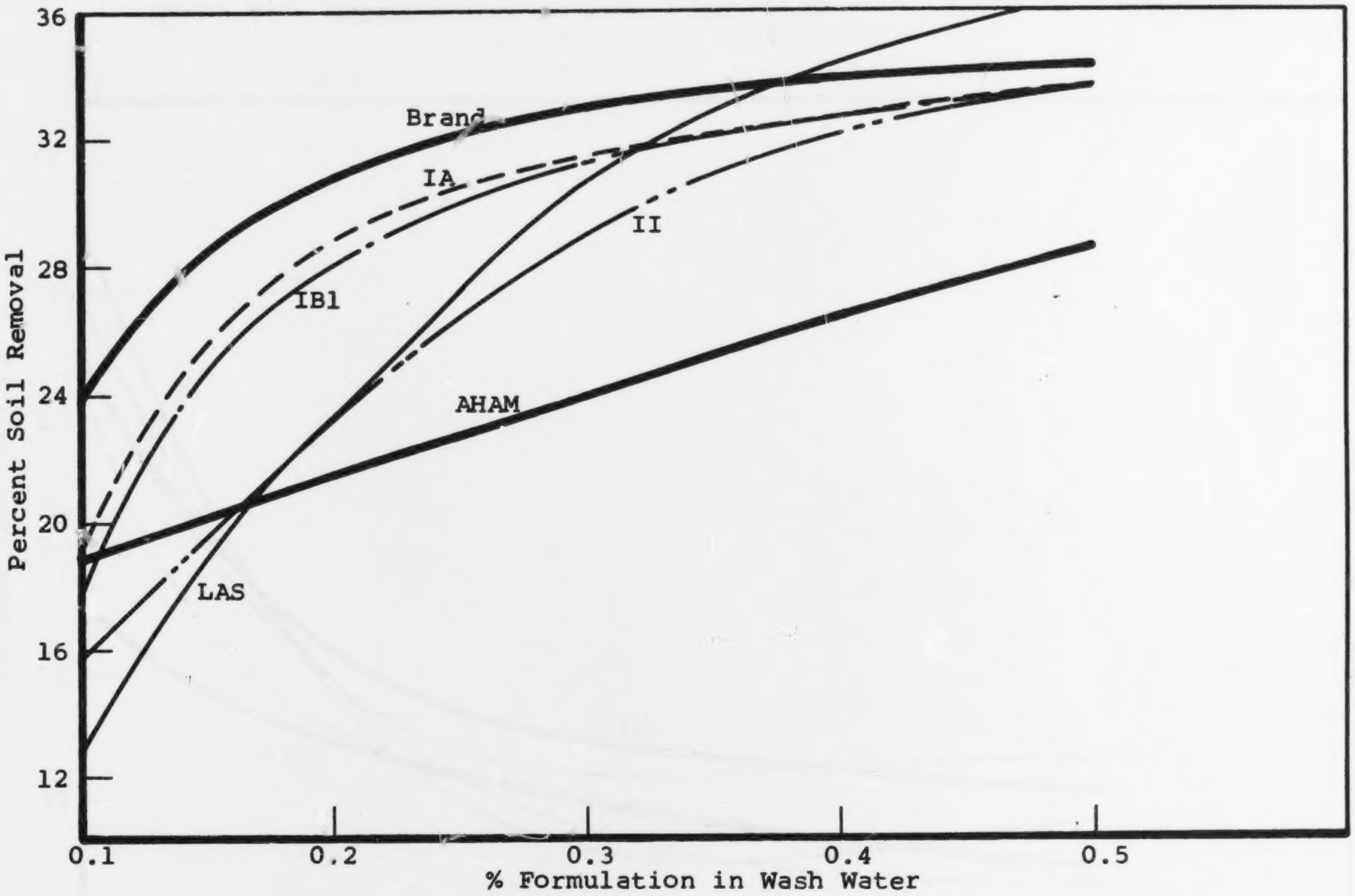
Graph 22. DETERGENCIES OF TEST FORMULATIONS "G" AT 300 PPM HARDNESS



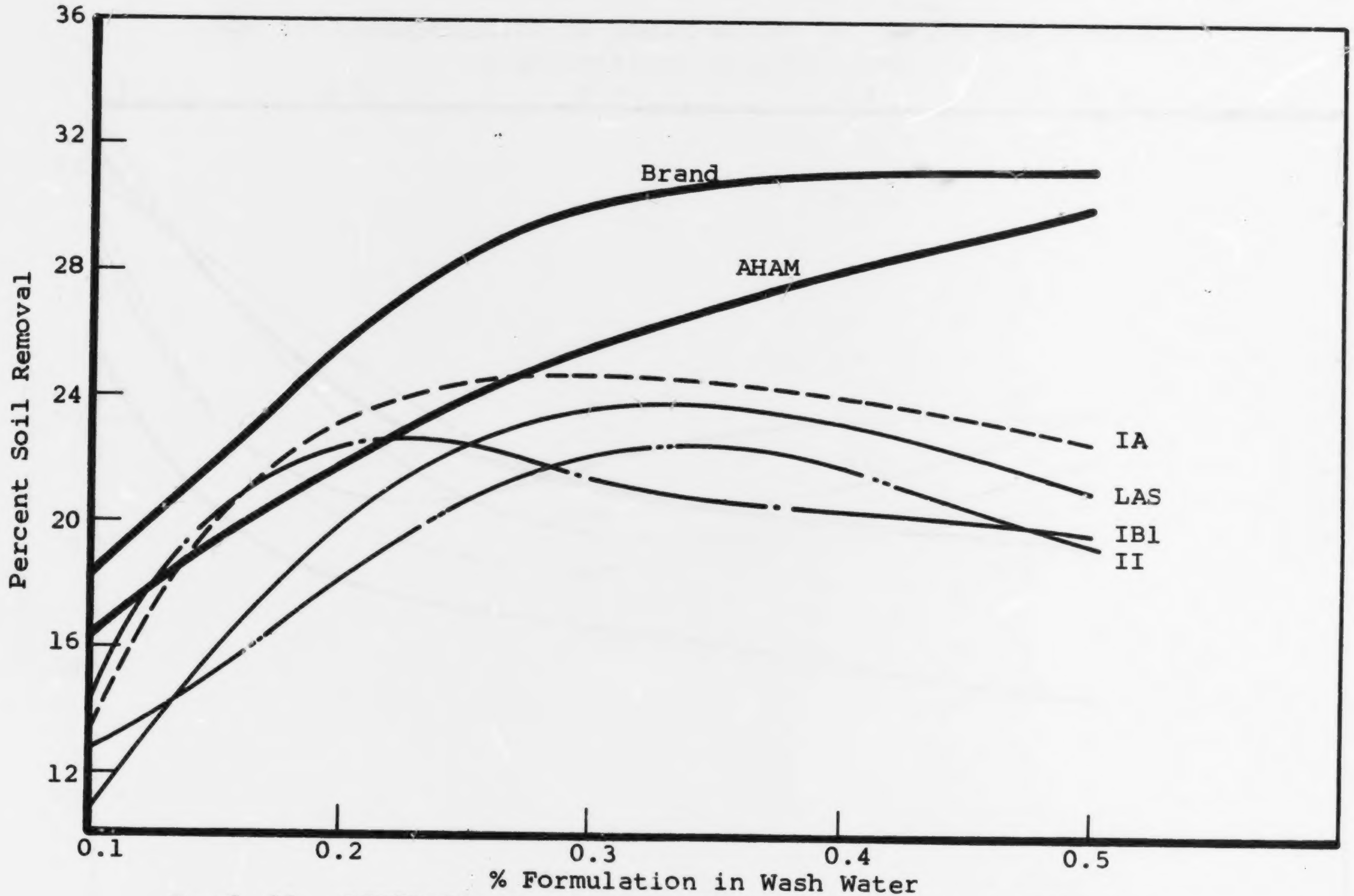
Graph 23. DETERGENCIES OF TEST FORMULATIONS "H" AT 50 PPM HARDNESS



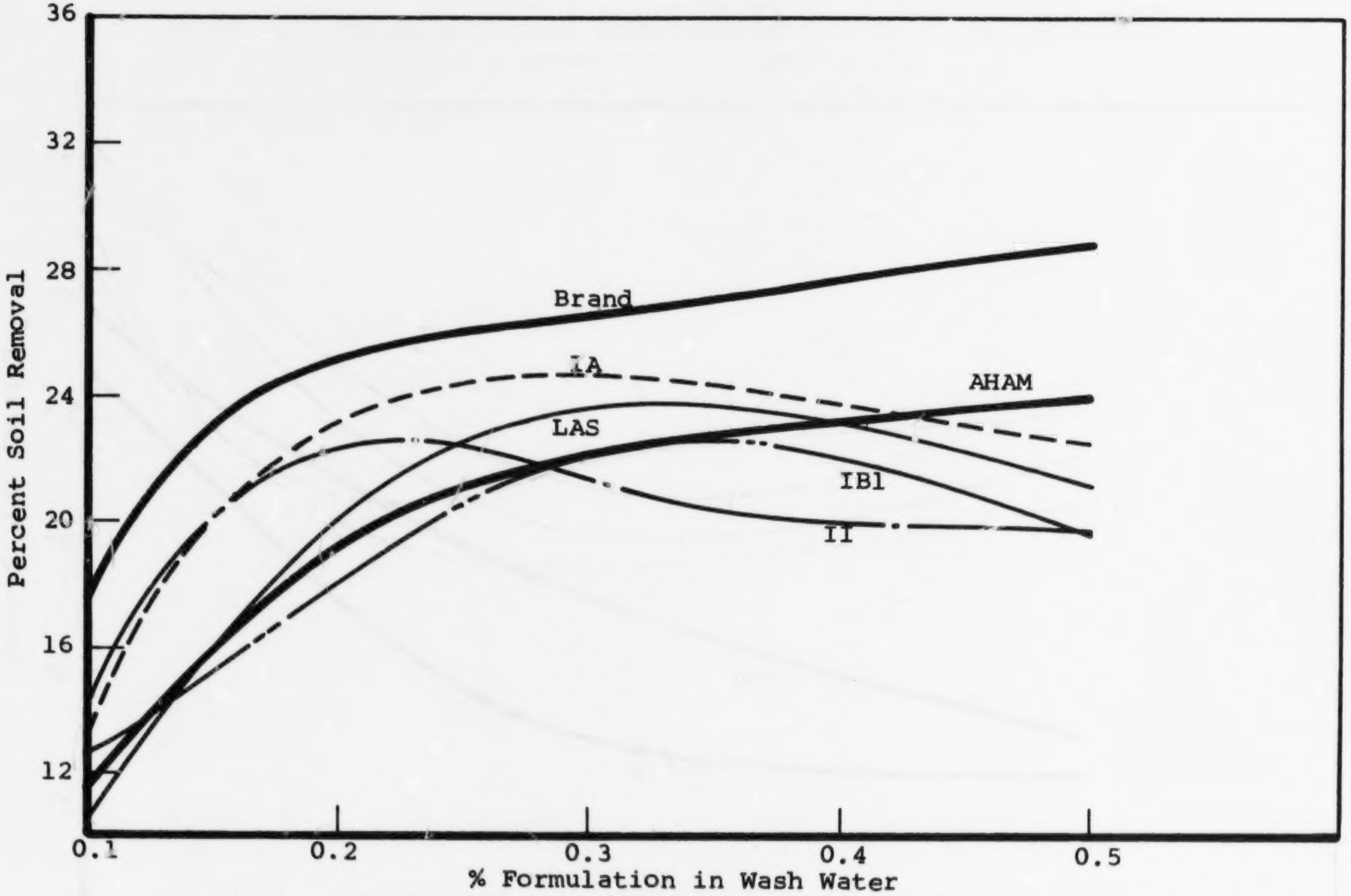
Graph 24. DETERGENCIES OF TEST FORMULATIONS "H" AT 135 PPM HARDNESS



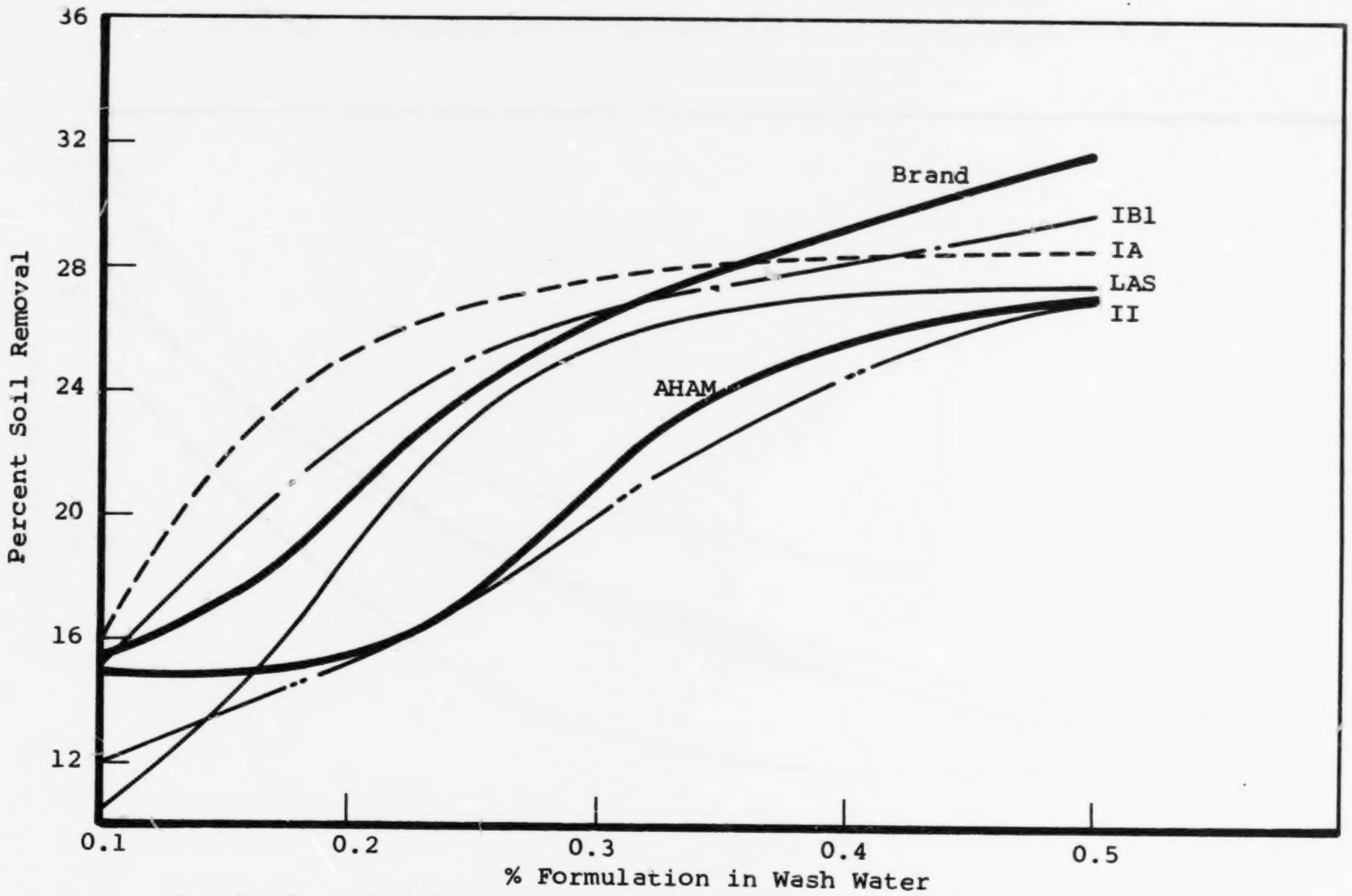
Graph 25. DETERGENCIES OF FORMULATIONS "H" AT 300 PPM HARDNESS



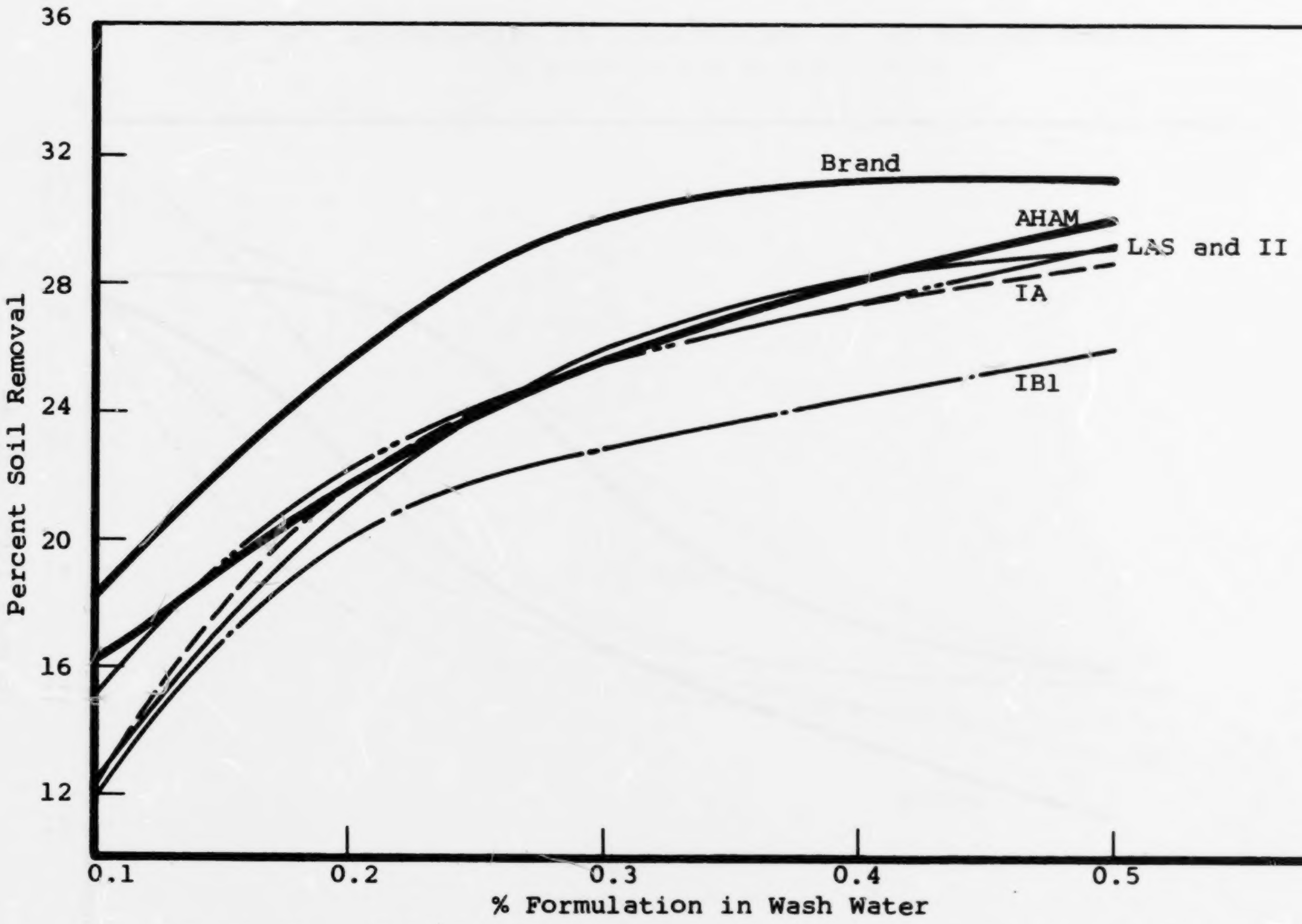
Graph 26. DETERGENCIES OF FORMULATIONS "I" AT 50 PPM HARDNESS



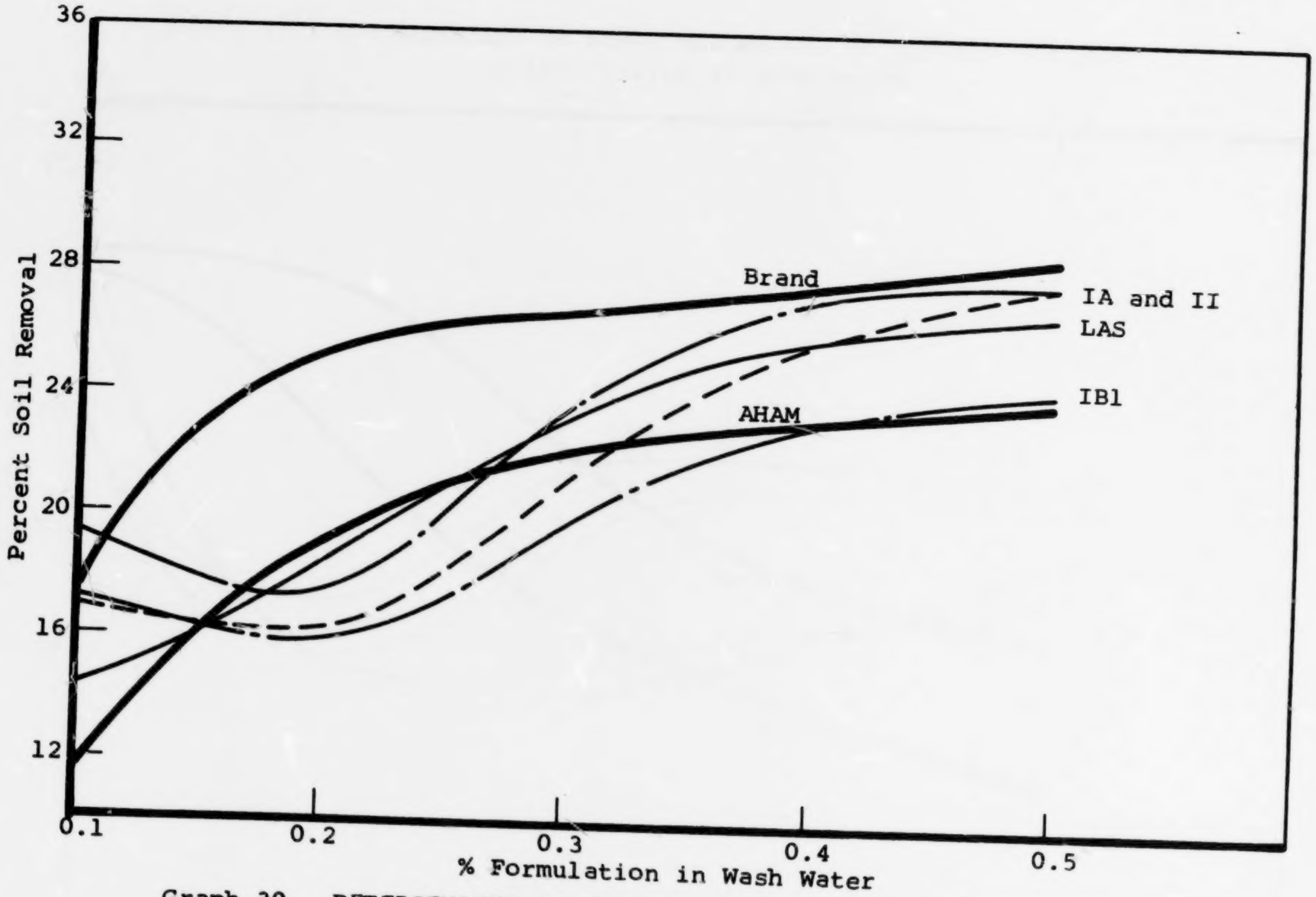
Graph 27. DETERGENCIES OF FORMULATIONS "I" AT 135 PPM HARDNESS



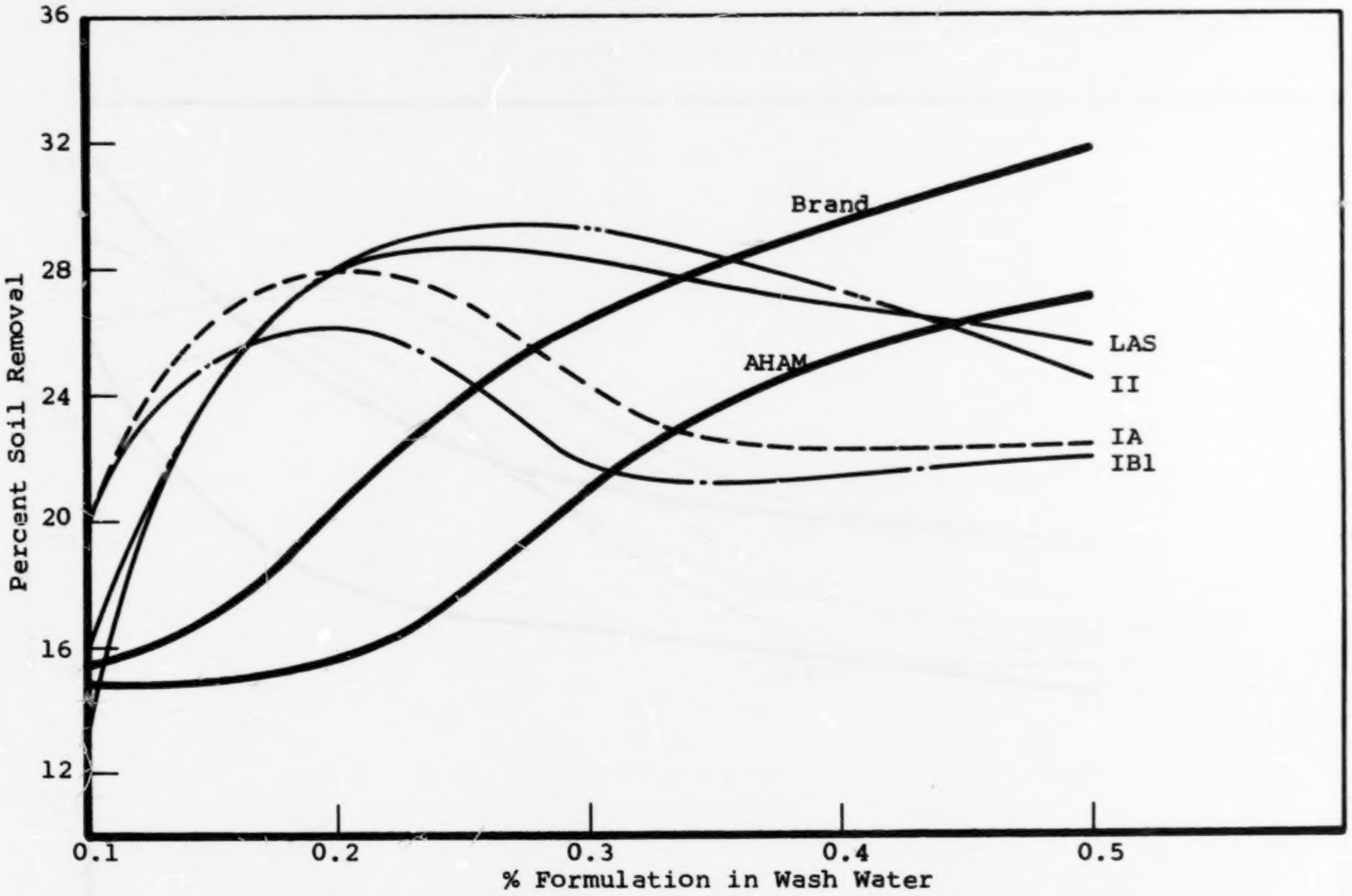
Graph 28. DETERGENCIES OF FORMULATIONS "I" AT 300 PPM HARDNESS



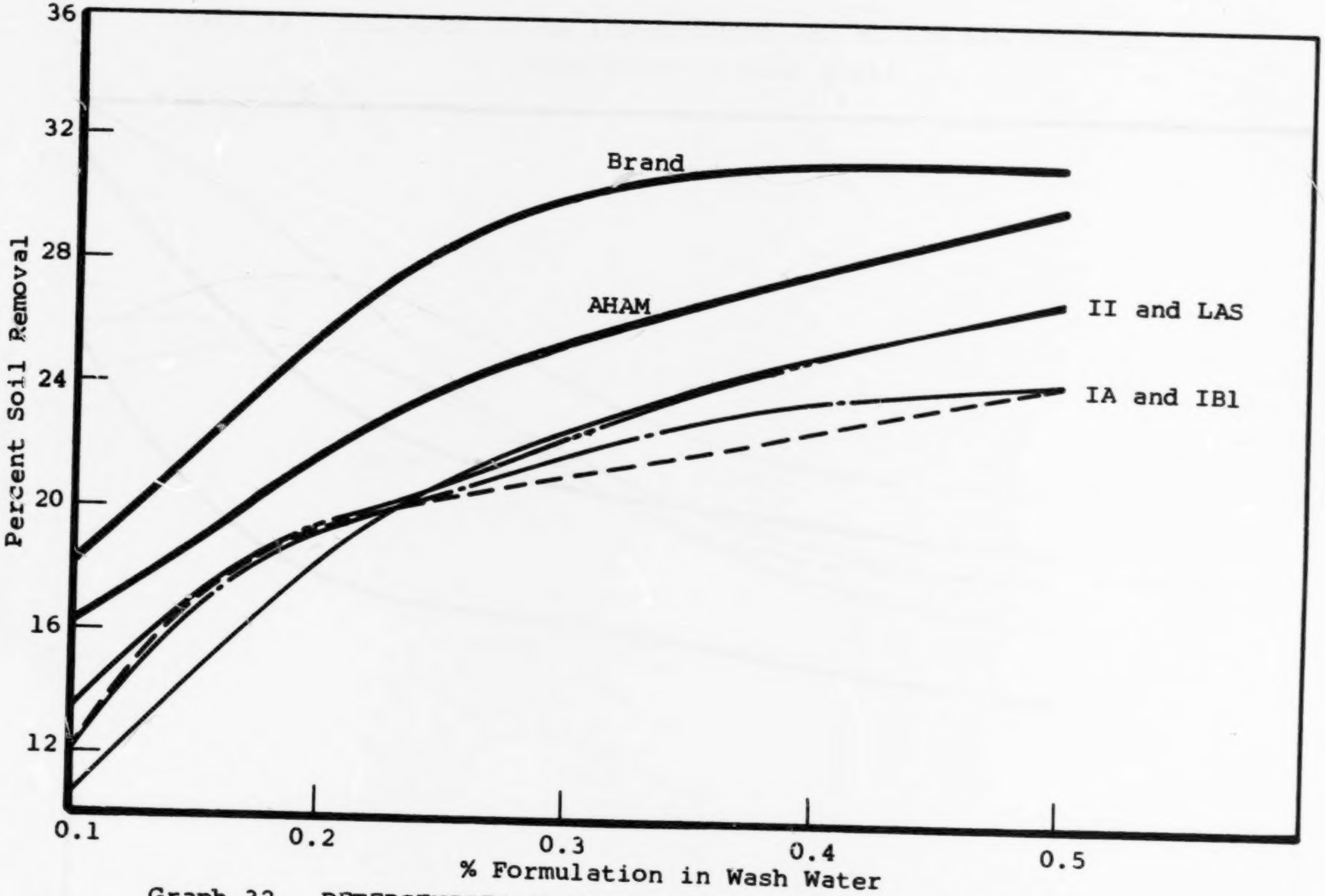
Graph 29. DETERGENCIES OF FORMULATIONS "J" AT 50 PPM HARDNESS



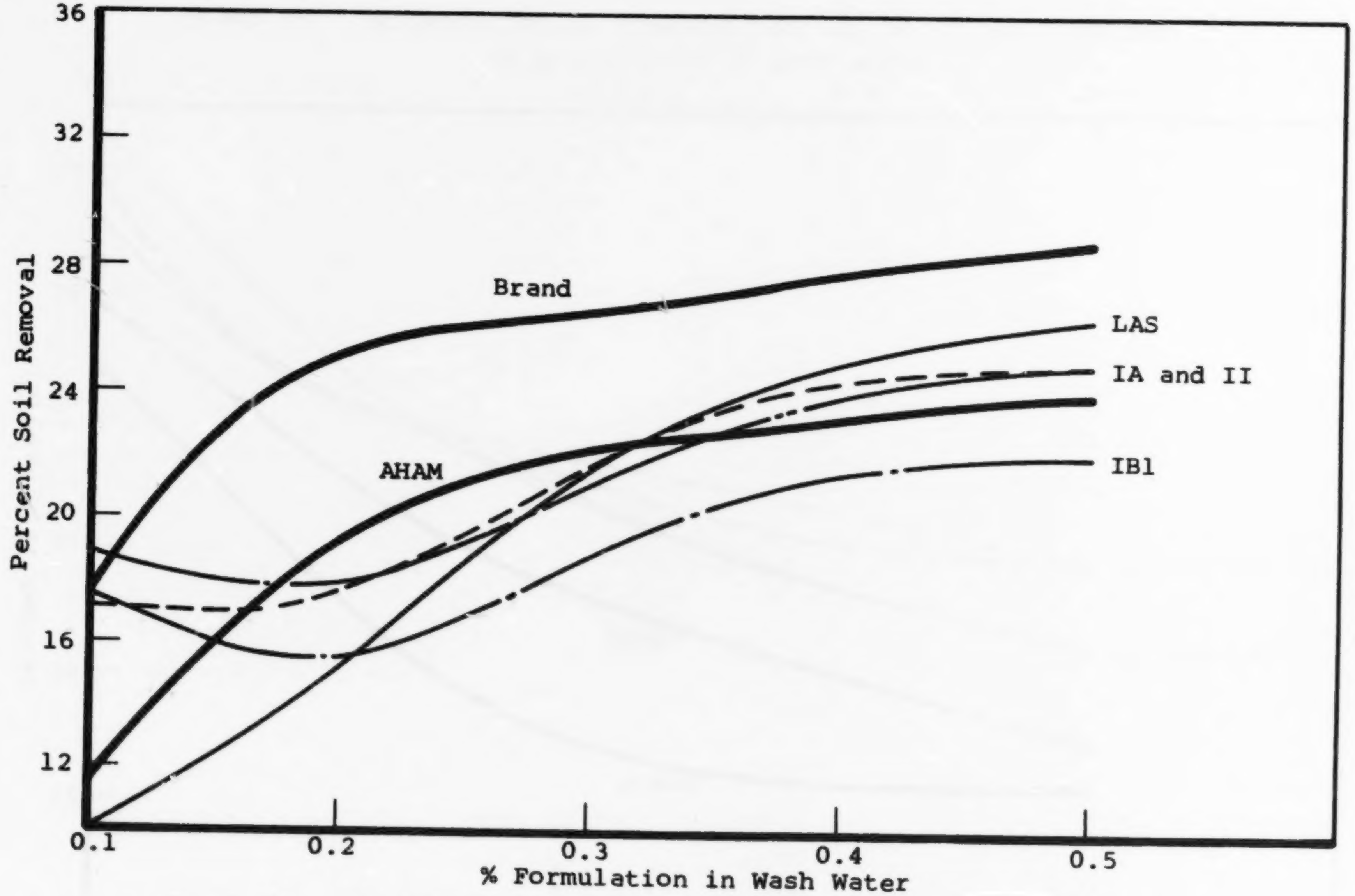
Graph 30. DETERGENCIES OF FORMULATIONS "J" AT 135 PPM HARDNESS



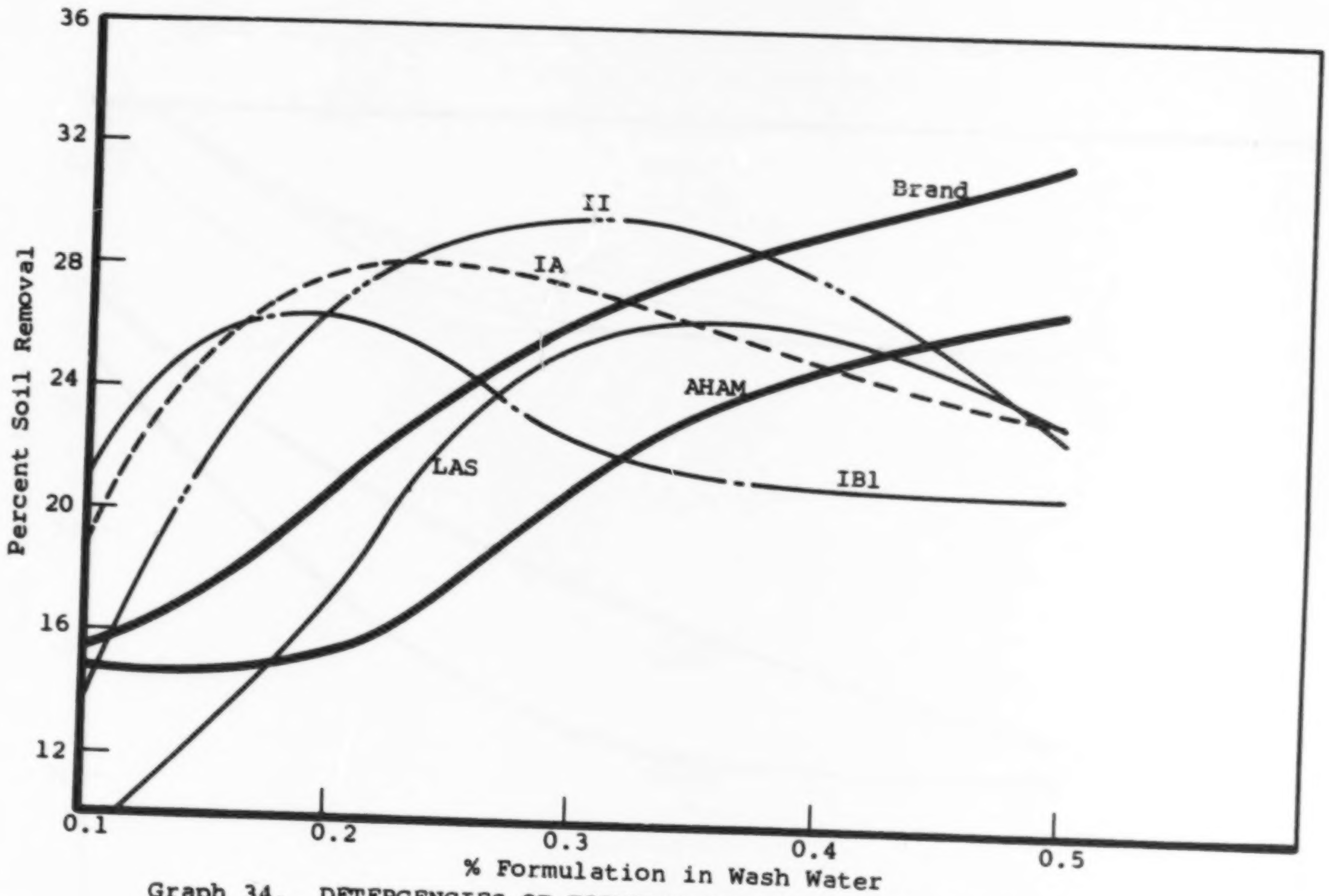
Graph 31. DETERGENCIES OF FORMULATIONS "J" AT 300 PPM HARDNESS



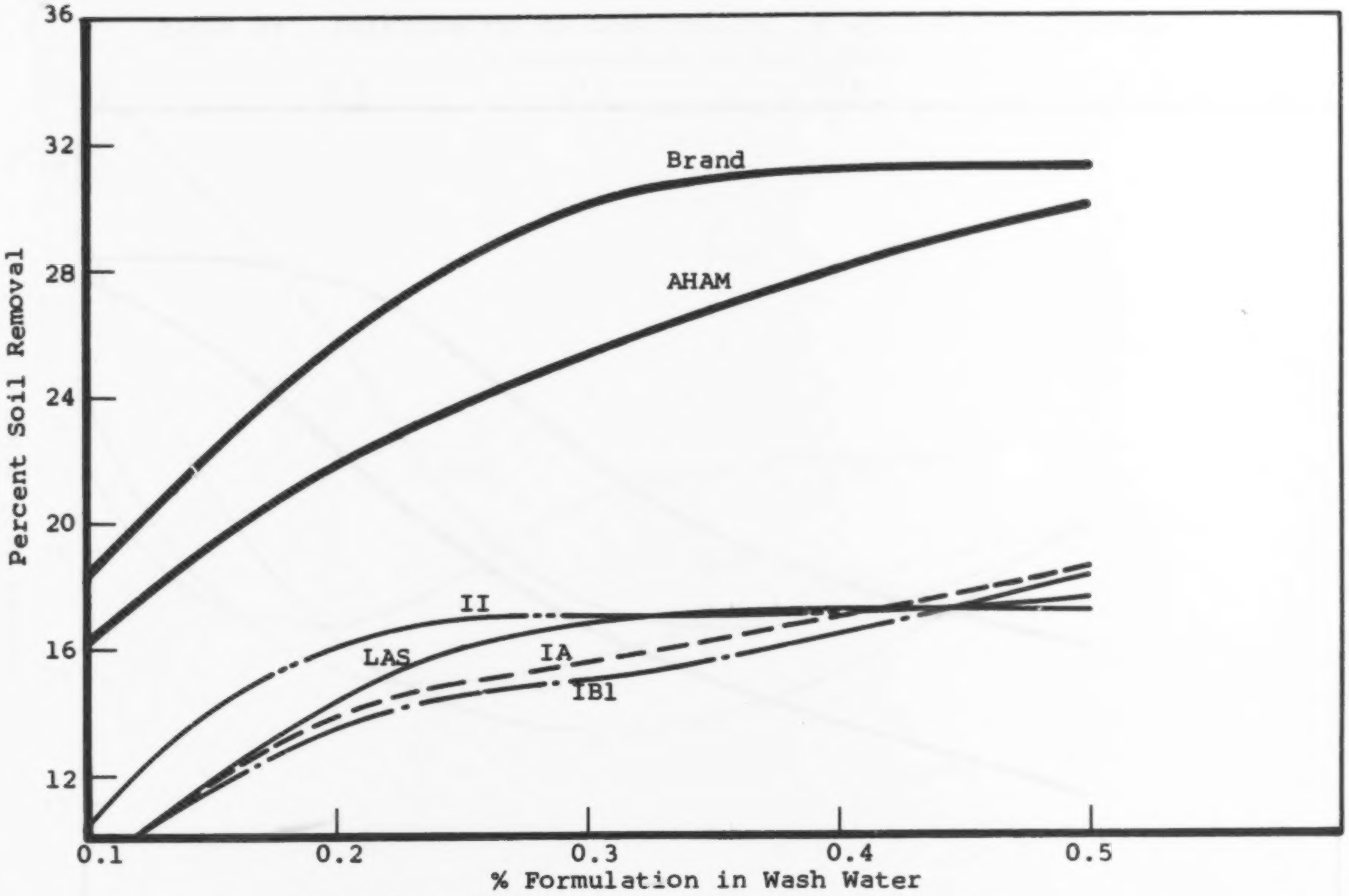
Graph 32. DETERGENCIES OF FORMULATIONS "K" AT 50 PPM HARDNESS



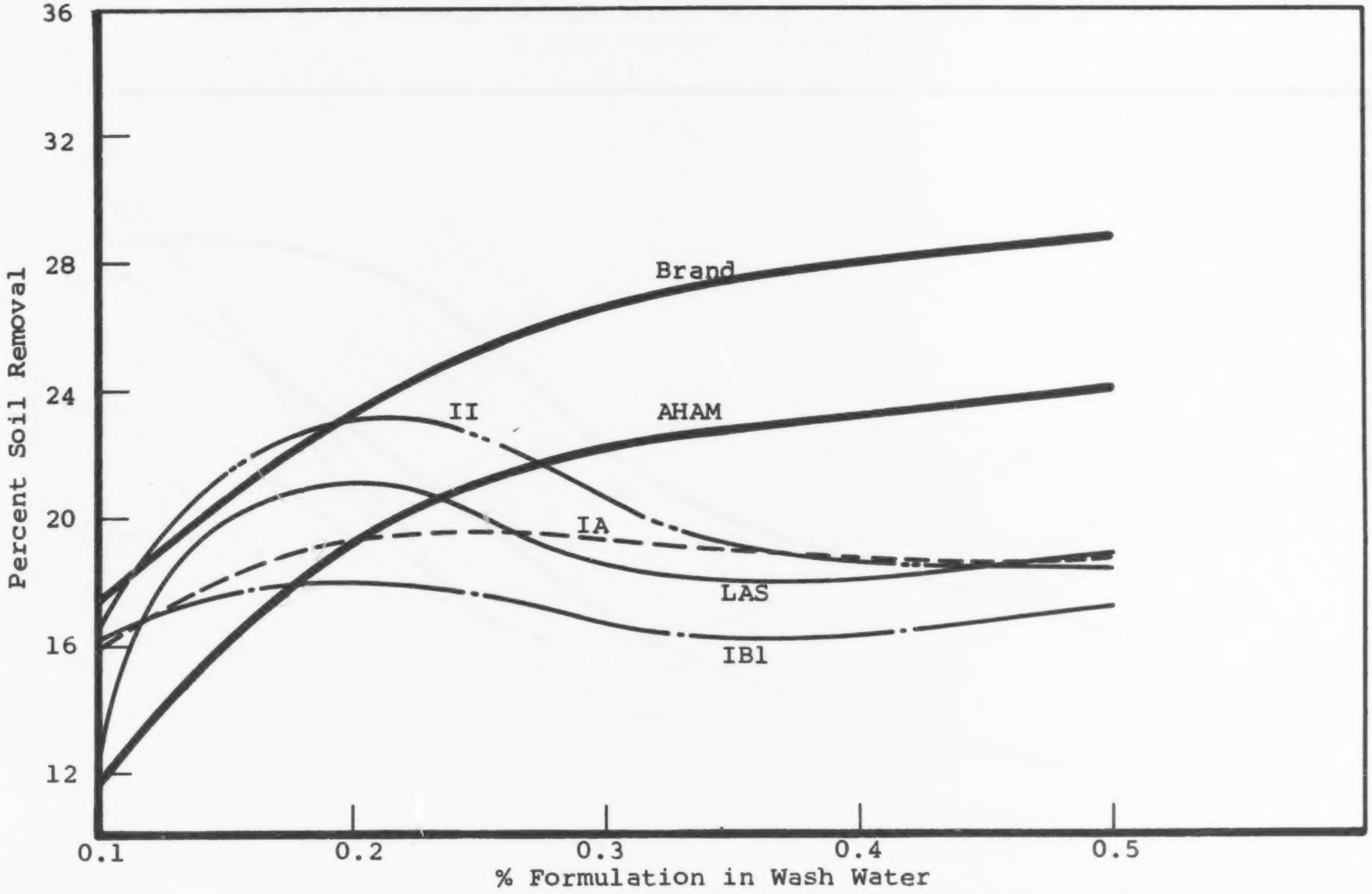
Graph 33. DETERGENCIES OF FORMULATIONS "K" AT 135 PPM HARDNESS



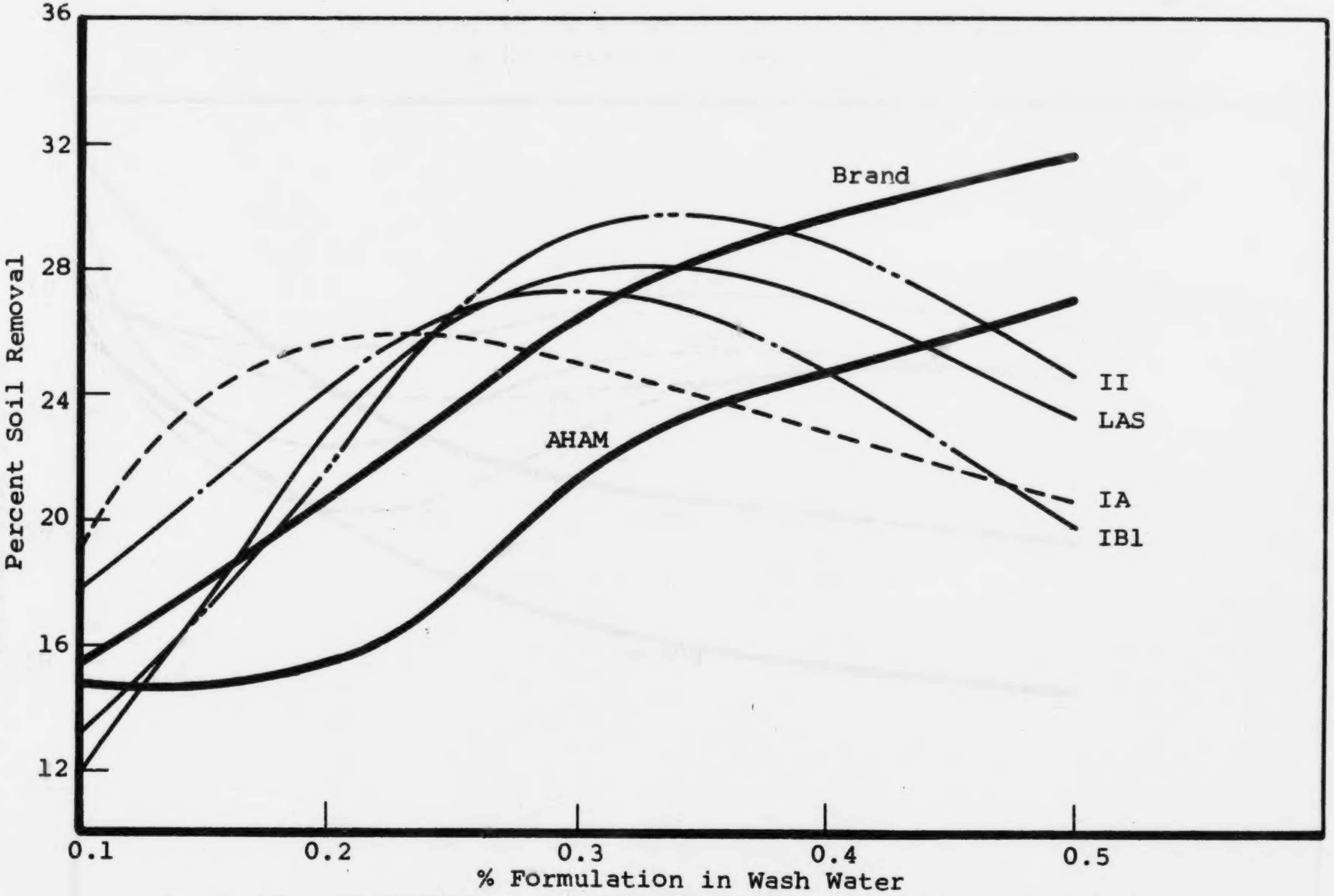
Graph 34. DETERGENCIES OF FORMULATIONS "K" AT 300 PPM HARDNESS



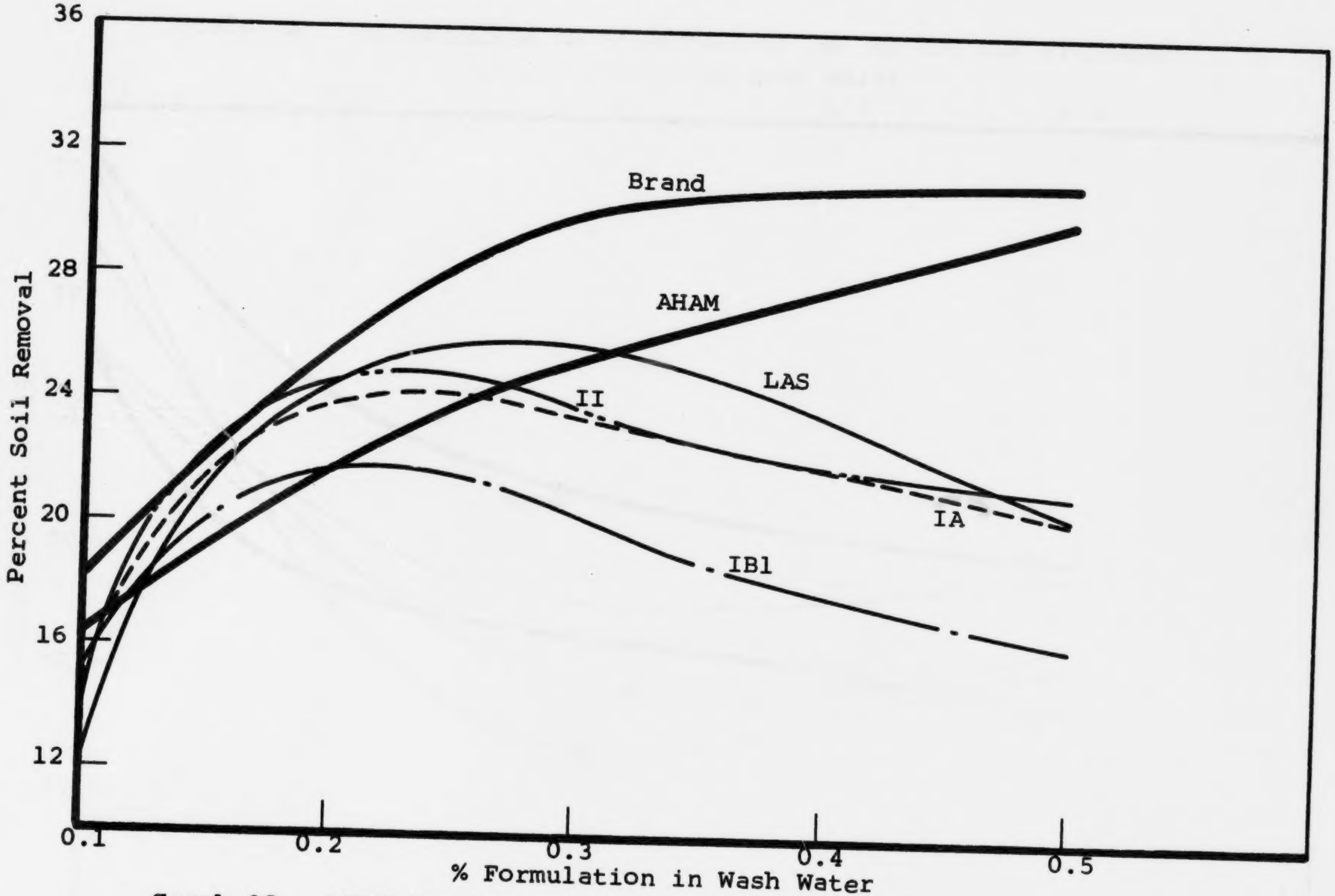
Graph 35. DETERGENCIES OF FORMULATIONS "L" AT 50 PPM HARDNESS



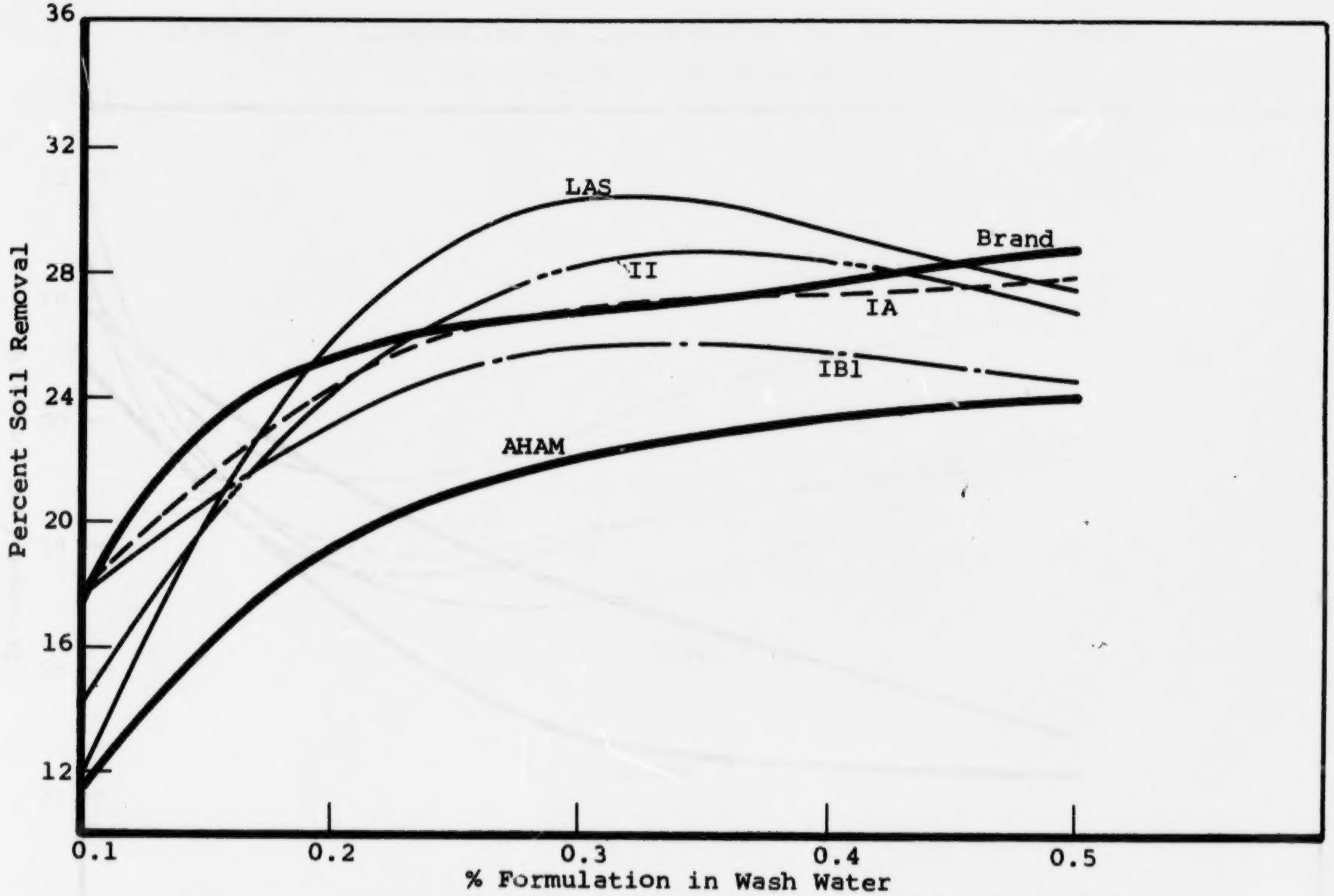
Graph 36. DETERGENCIES OF FORMULATIONS "L" AT 135 PPM HARDNESS



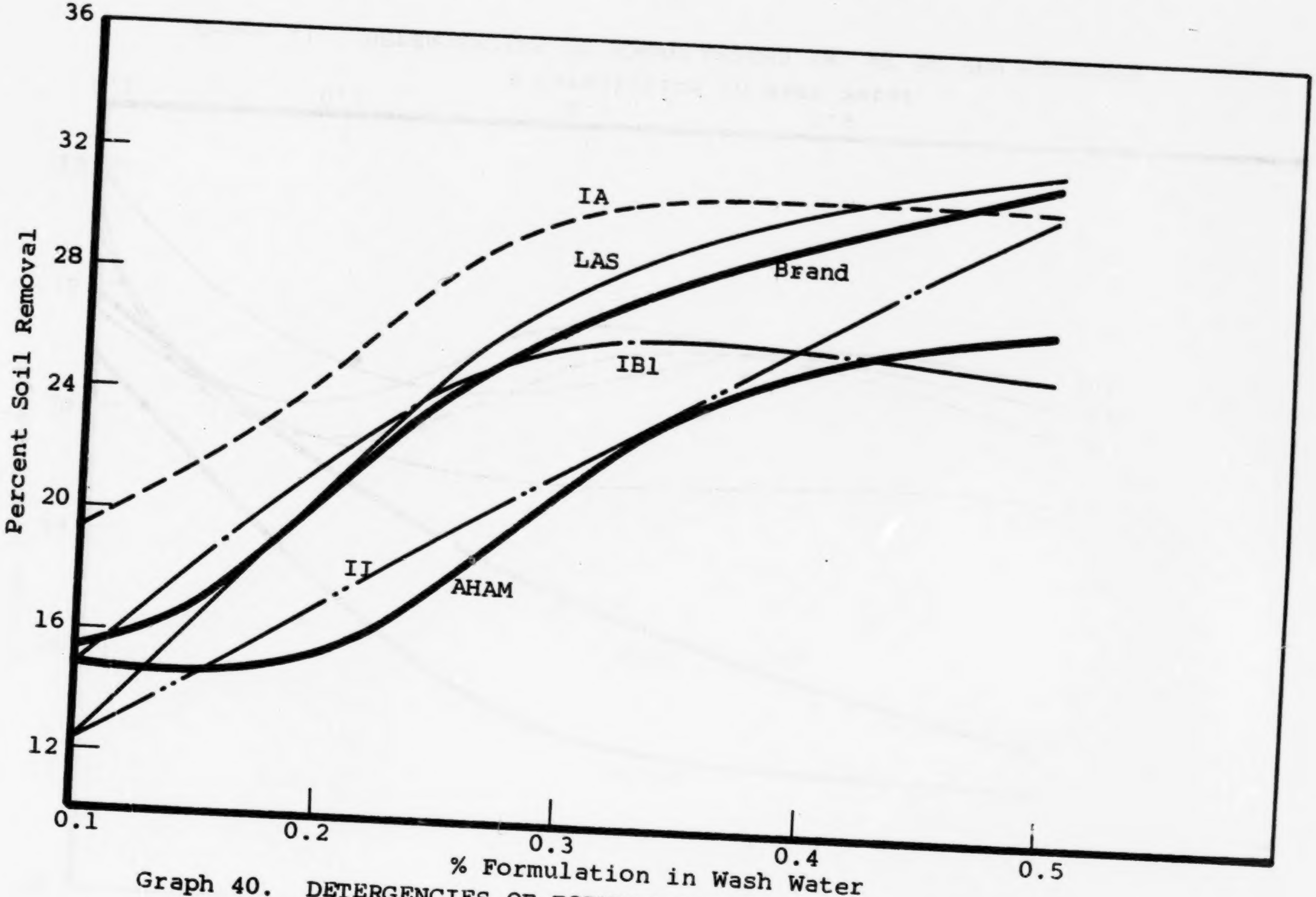
Graph 37. DETERGENCIES OF FORMULATIONS "L" AT 300 PPM HARDNESS



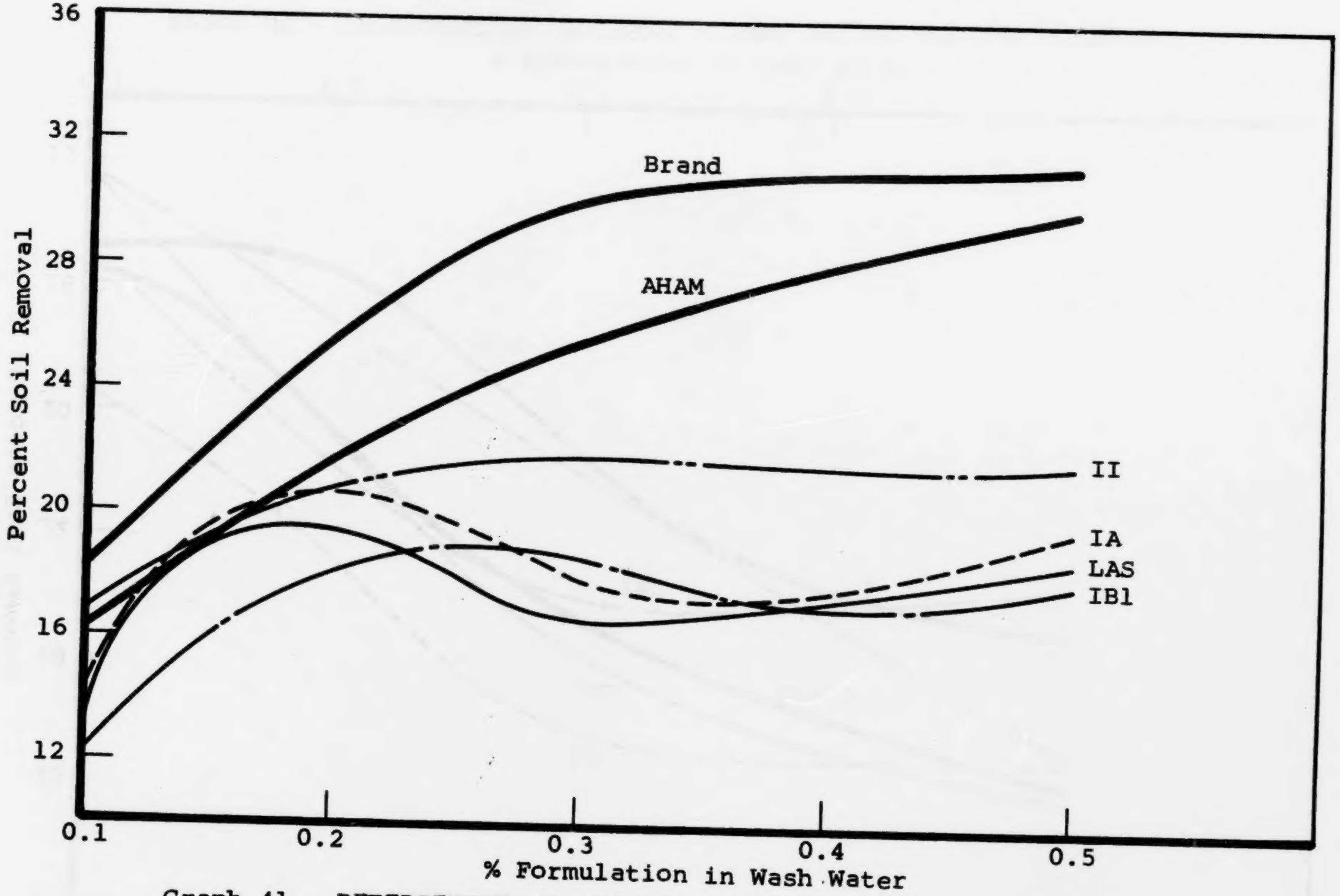
Graph 38. DETERGENCIES OF FORMULATIONS "M" AT 50 PPM HARDNESS



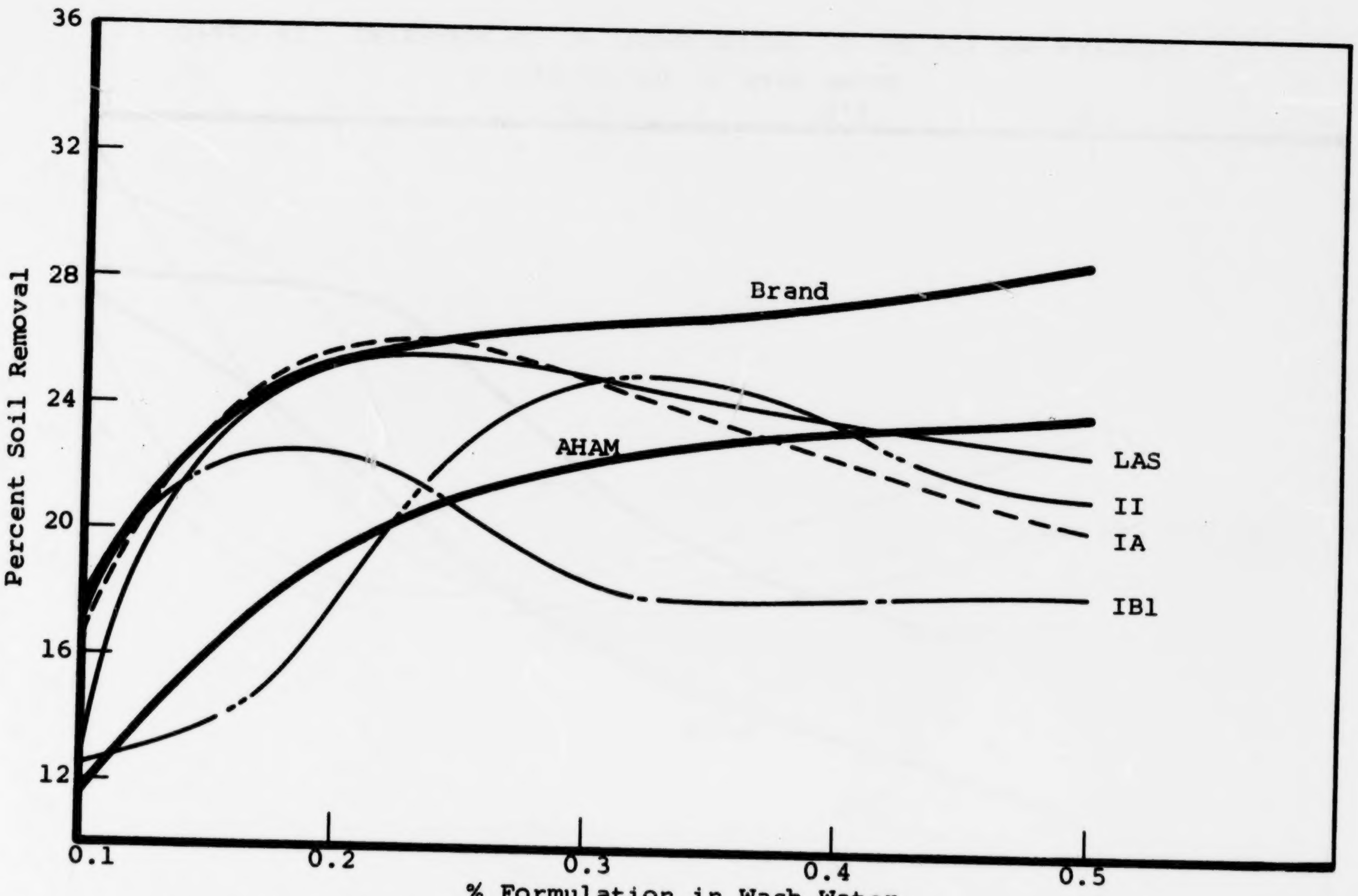
Graph 39. DETERGENCIES OF FORMULATIONS "M" AT 135 PPM HARDNESS



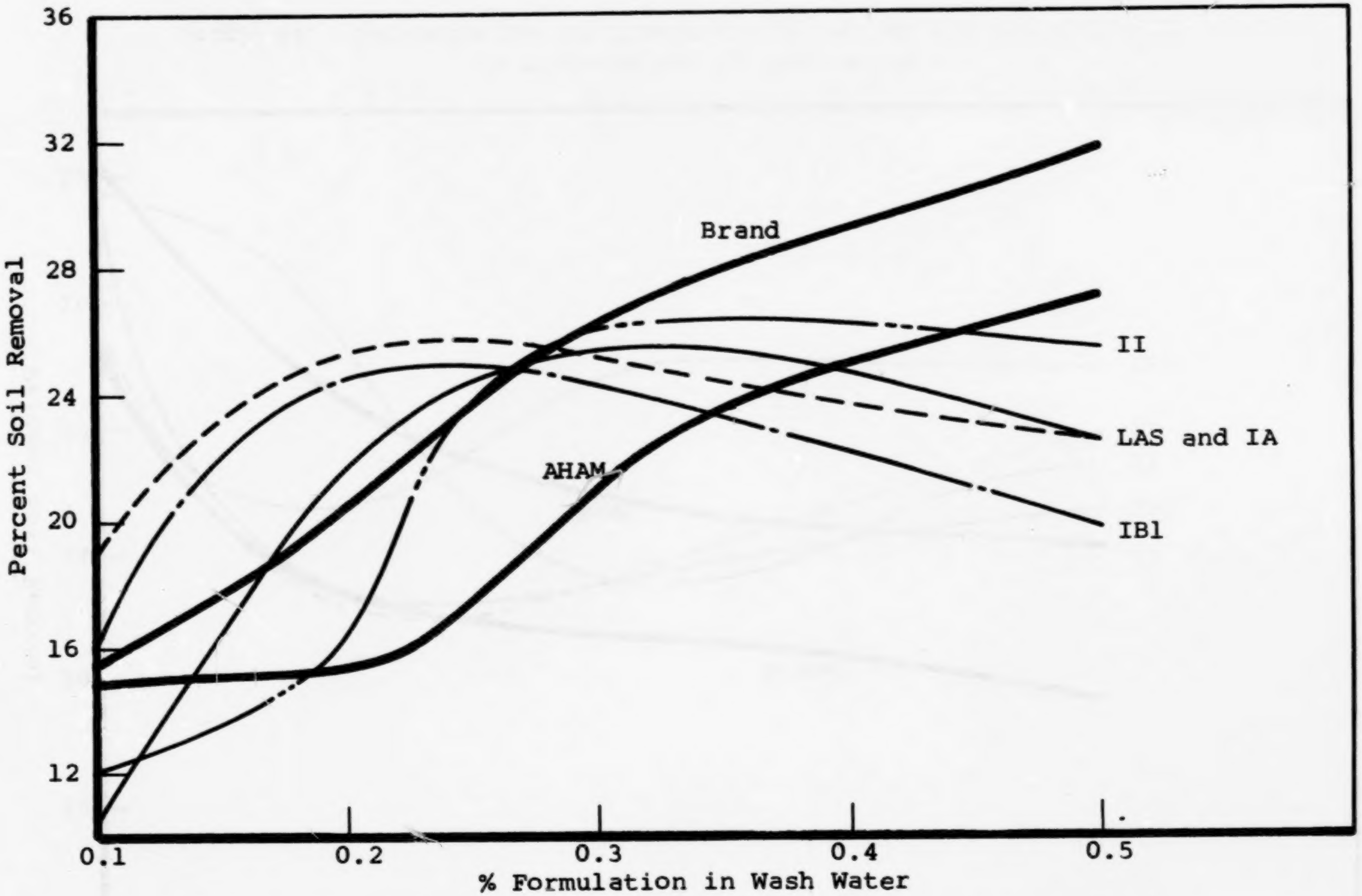
Graph 40. DETERGENCIES OF FORMULATIONS "M" AT 300 PPM HARDNESS



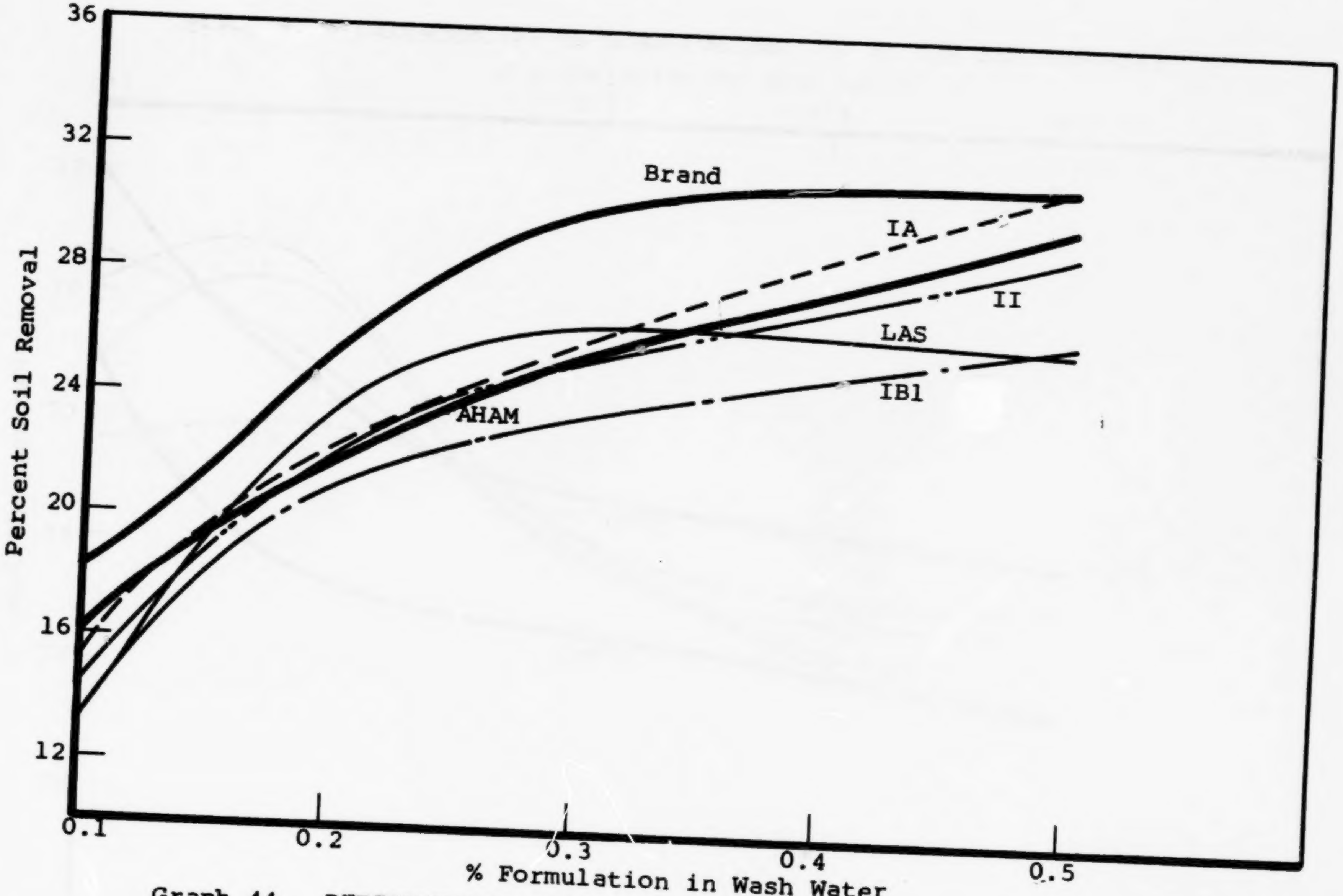
Graph 41. DETERGENCIES OF FORMULATIONS "N" AT 50 PPM HARDNESS



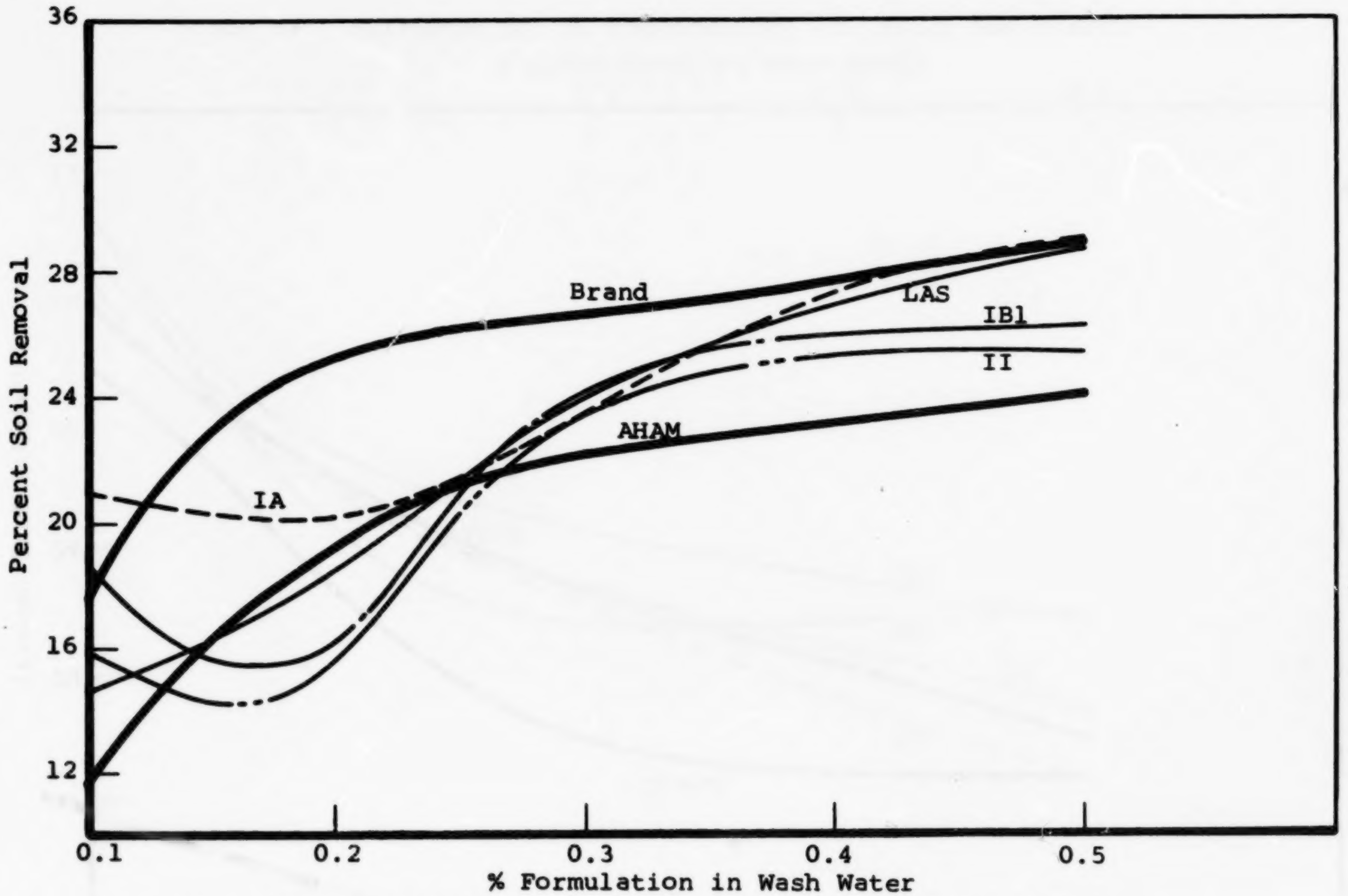
Graph 42. DETERGENCIES OF FORMULATIONS "N" AT 135 PPM HARDNESS



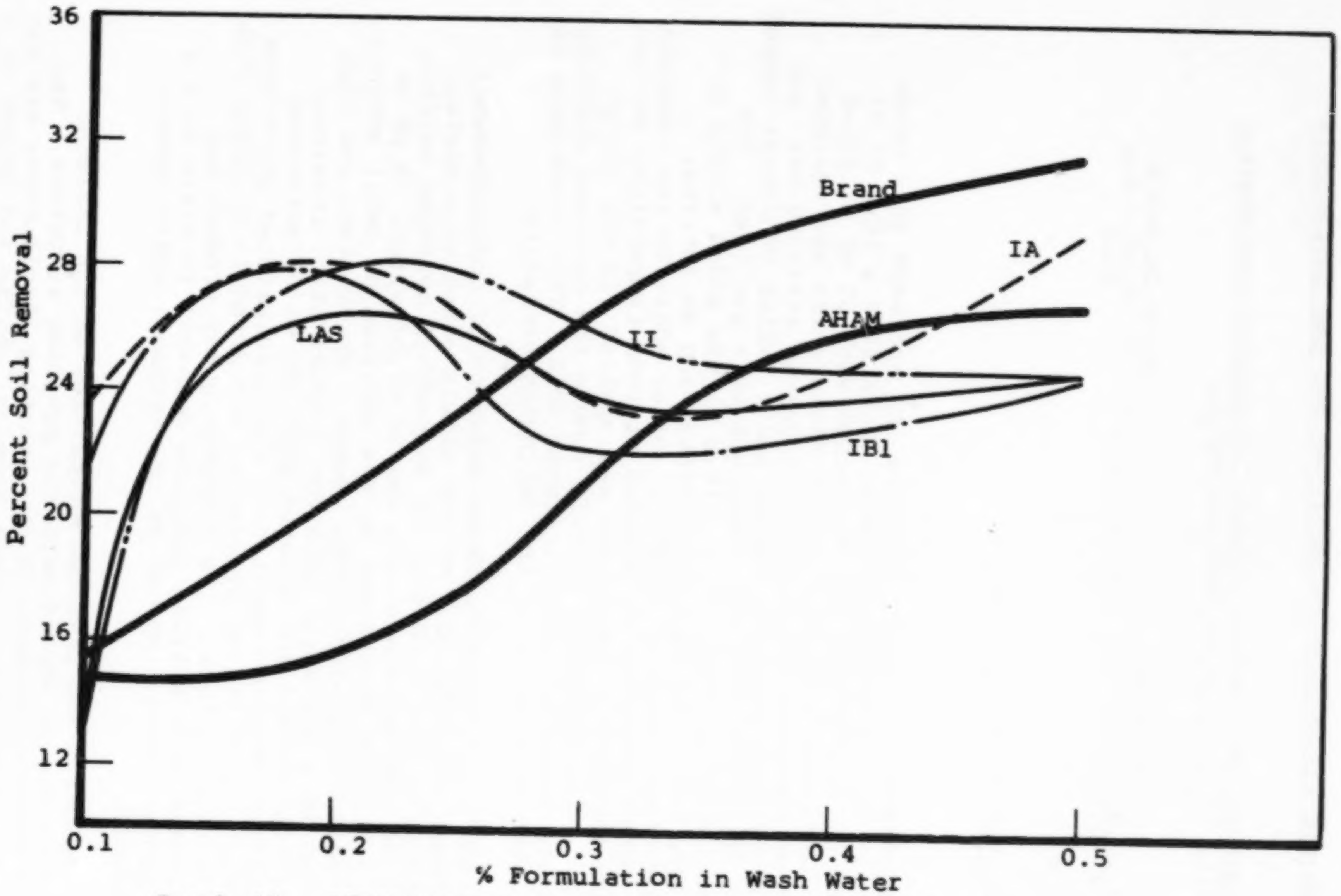
Graph 43. DETERGENCIES OF FORMULATIONS "N" AT 300 PPM HARDNESS



Graph 44. DETERGENCIES OF FORMULATIONS "O" AT 50 PPM HARDNESS



Graph 45. DETERGENCIES OF FORMULATIONS "O" AT 135 PPM HARDNESS



Graph 46. DETERGENCIES OF FORMULATIONS "O" AT 300 PPM HARDNESS

Synthetic Procedures and Analyses for the Surfactants

Surfactant IA: Sodium dodecylbenzenesulfonamidoethyl sulfate ($C_{12}H_{25}C_6H_4SO_2NHCH_2CH_2OSO_3Na$)

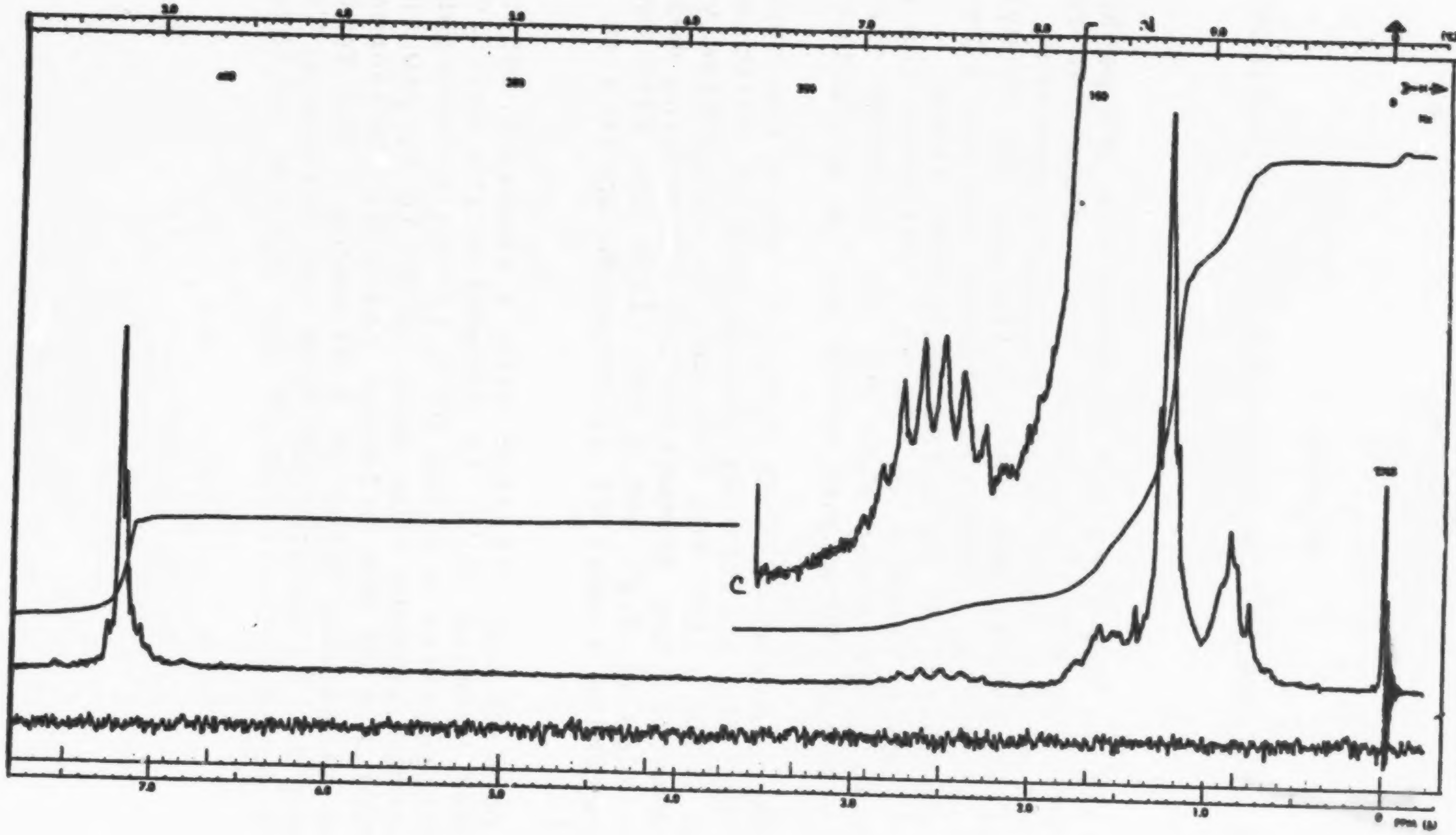
$$\underset{\underline{a}}{C_{12}H_{25}C_6H_5} \xrightarrow{2ClSO_3H} \underset{\underline{b}}{C_{12}H_{25}C_6H_4SO_2Cl} \xrightarrow[\text{Base}]{NH_2CH_2CH_2OSO_3H}$$

$$\underset{\text{IA}}{C_{12}H_{25}C_6H_4SO_2NHCH_2CH_2OSO_3Na}$$

Dodecylbenzenesulfonyl chloride (b) was used as a crude mixture in 1,2-dichloroethane. Thus 24.6 g (0.1 m) of dried dodecylbenzene (a) was mixed with 33 ml of dried 1,2-dichloroethane in a 3-neck flask which was equipped with an internal thermometer, magnetic stirring bar, gas equilibrating dropping funnel and a reflux condenser topped with an outlet tube and connected to a gas trap. The chlorosulfonic acid, 23.3 g (0.2 m) was added slowly with cooling and stirring while maintaining an internal temperature range of 22-28°C. After addition was complete, the amber solution was stirred at room temperature for two hours and gentle aspiration was applied via the outlet tube on the condenser to help remove the hydrogen chloride and any unreacted chlorosulfonic acid. This crude mixture was then used as is in the following procedure.

The above 1,2-dichloroethane solution of dodecylbenzenesulfonyl chloride (0.1 m) was slowly added to a mixture containing 28.2 g (0.2 m) of aminoethyl hydrogen sulfate, 45 g of sodium bicarbonate and 50 ml of water. A pH of 7.5 - 8.0 was maintained by the addition of small amounts of sodium bicarbonate when needed. The mixture was then heated in a hot water bath for 2 hours with occasional stirring, cooled and diluted with 600 ml of saturated potassium chloride solution. The precipitated gelatinous product was filtered by gravity and dried in a vacuum oven at 50-60°C/13 torr. The somewhat gummy product was extracted with boiling absolute methanol to yield 33.4 g of product after removal of the methanol under reduced pressure.

The spectral and physical properties of the isolated product are in accord with the proposed structure. The five aromatic protons of the starting alkylbenzene are not greatly different in their chemical shifts and appear as a "close" multiplet centered at 432 Hz (PMR Spectrum No. 1). On the other hand, the four aromatic protons of the para-sulfonyl-alkylbenzene are best represented as an AA'XX'



60 MC NMR
SPECTRUM NO. NMR SPECTRUM No. 1

OPERATOR [illegible] DATE 7/21/[illegible]

SAMPLE Nalkylene 500
(Dodecylbenzene, Conoco)

$C_{11}H_{23}CH_2-C_6H_5$

	A	B		C
SOLVENT	Silicone-C			
TEMPERATURE	—	—	°C	—
FILTER BANDWIDTH	4.0	2.0	cps	1.0
R.F. FIELD	0.04	0.04	mG	0.16
SWEEP TIME	500	250	sec	500
SWEEP WIDTH	500	500	cps	500
SWEEP OFFSET	0	500	cps	0
SPECTRUM AMP.	2.5	10.0		50.0
INTEGRAL AMP.				

REMARKS: 10% Conc.

VARIAN associates CHART 100-C

spin system (Figure 1) and would be expected to show the two areas of absorption which are seen in the spectrum of the product (PMR Spectrum No. 2).

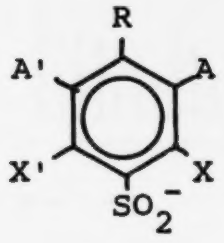


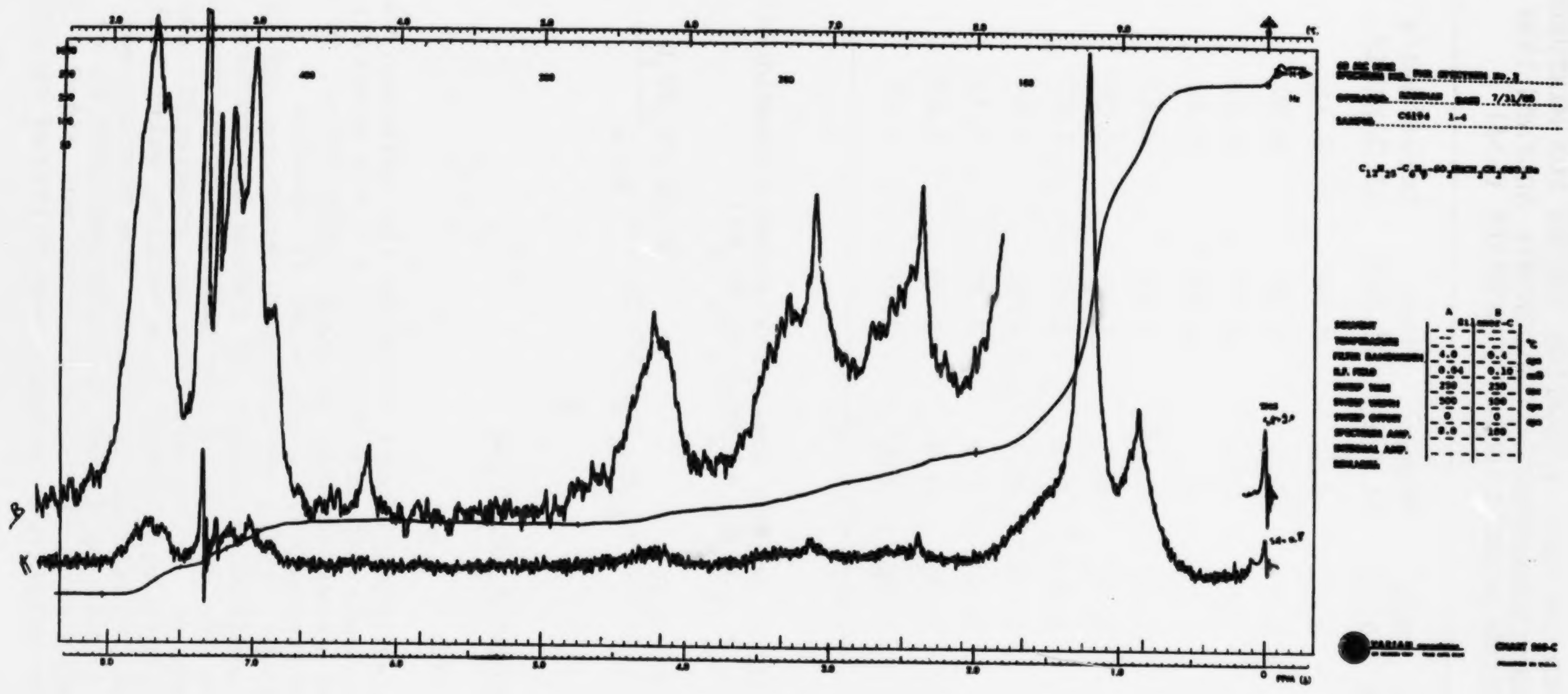
Figure 1

PROTON ASSIGNMENTS OF PARA SULFONYL-ALKYLBENZENE

Moving upfield in the spectrum (towards the tms peak) the increased spectrum amplitude sweep ("B") shows the region of absorption of the sulfonamido methylene protons ($-SO_2NH-C\underline{H}_2$) at 190 Hz and that of the sulfate methylene ($-C\underline{H}_2OSO_3^-$) at 250 Hz. The hydrocarbon protons appear in the region of 50-100 Hz with the phenylmethylene ($-C\underline{H}_2-C_6H_4-$) being visible at 150 Hz. Although the proton integration is quite acceptable for the assigned structure, the normally broad $-N\underline{H}$ signal could not be accounted for.

The infrared spectrum of this material shows the symmetric and asymmetric SO_2 stretching absorptions of sulfonamide at 8.62 and 7.55μ (1160 and 1325 cm^{-1}), respectively. The probable symmetric and asymmetric SO_2 stretching modes of sulfate are seen at 8.85 and 6.82μ (1130 and 1466 cm^{-1}). The N-H stretching signal of sulfonamido appears at 3.17μ (3155 cm^{-1}).

The dried product was titrated with a standard cation (Rohm & Haas' Hyamine 1622) to determine its anion content. Pure product requires a titre of 2.12 meq/g, whereas sodium dodecylbenzenesulfonate (the most probable by-product from simple hydrolysis of the sulfonyl chloride) possesses a theoretical titration value of 2.87 meq/g. The found titre was 2.24 meq/g. As determined from the following Table, the product could contain 86% of the desired sulfate, IA.


7/31/80
C6194 1-4
A
B
4.0
0.4
0.04
0.10
250
250
500
500
0
0
8.0
100
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)
500
400
300
200
100
0
B
K

CALCULATED CATIONIC TITRATION VALUES FOR MIXTURES SODIUM DODECYLBENZENESULFONAMIDOETHYL SULFATE (IA) AND SODIUM DODECYLBENZENESULFONATE (LAS)

Grams of IA	Meq of I	Grams of LAS	Meq of LAS	Total meq/g of Mixture
1.0	2.12	0.0	0.00	2.12
0.9	1.91	0.1	0.29	2.20
0.8	1.70	0.2	0.57	2.27
0.7	1.48	0.3	0.86	2.34
0.6	1.27	0.4	1.15	2.42
0.5	1.06	0.5	1.44	2.50
0.4	0.85	0.6	1.72	2.57
0.3	0.64	0.7	2.01	2.65
0.2	0.42	0.8	2.30	2.72
0.1	0.21	0.9	2.59	2.80
0.0	0.00	1.0	2.87	2.87

Surfactant IB1: Sodium dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}-C_6H_4-SO_2NHCH_2CH_2SO_3Na$)

$$\underset{\underline{a}}{C_{12}H_{25}C_6H_5} \xrightarrow{2ClSO_3H} \underset{\underline{b}}{C_{12}H_{25}C_6H_4SO_2Cl} \xrightarrow[\text{Base}]{NH_2CH_2CH_2SO_3H}$$

$$\underset{\text{IB1}}{C_{12}H_{25}C_6H_4SO_2NHCH_2CH_2SO_3Na}$$

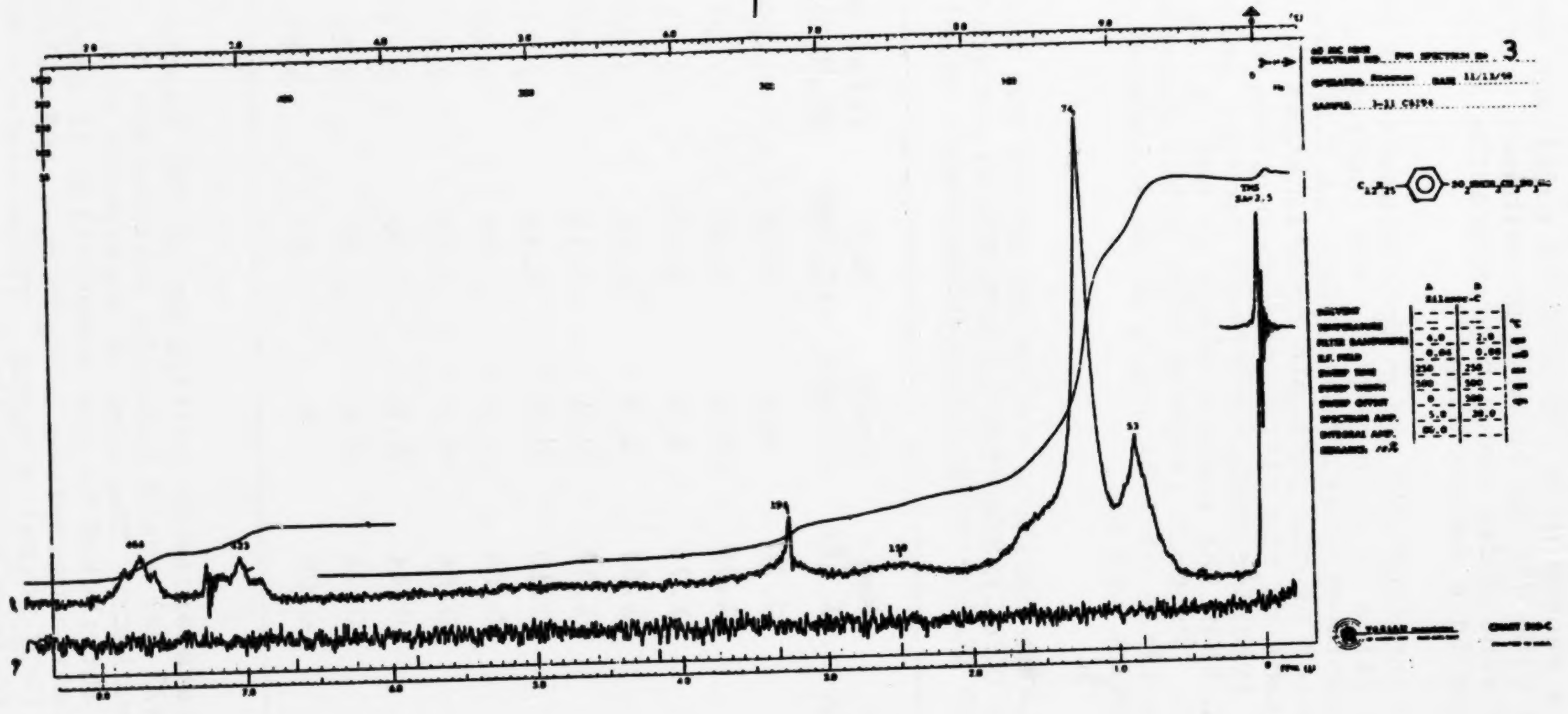
The dodecylbenzenesulfonyl chloride (b) solution was prepared as described previously. A 0.4 m quantity of this solution was slowly added, at room temperature, to a mixture containing 65.6 g (0.52 m) of taurine ($H_2NCH_2CH_2SO_3H$), 125 g of sodium bicarbonate and 175 ml of water. An additional amount of sodium bicarbonate was added during the course of the addition to maintain the pH between 7 and 8. After addition was completed, the reaction mixture was heated by a boiling water bath for 2 hours with occasional stirring. The mixture was then brought to a boil by direct heating and 1500 ml of saturated potassium chloride solution was added. After cooling, the gelatinous product was filtered by gravity, dried in a vacuum oven (50-60°C/13 torr) and the solid was extracted with 750 ml of boiling methanol. After removal of the solvent under reduced pressure the material was dried again in a vacuum oven.

Cationic titration for anion determination of this material yielded a value of 2.28 meq/g. The theoretical value for the sulfonamidoethylsulfonate (IB1) is 2.20 meq/g. Consideration of the probable contamination by LAS by-product leads to the titration values given in the following Table for fraction combinations of product and LAS, where it is seen that the product could be 88% of the desired surfactant. Product isolated from other procedures supplied a titre of 2.54 meq/g which indicated that 50% of the product was LAS.

CALCULATED CATIONIC TITRATION VALUES FOR MIXTURES OF SODIUM DODECYLBENZENESULFONAMIDOETHYLSULFONATE (IB1) AND SODIUM DODECYLBENZENESULFONATE (LAS)

Grams of IB1	Meq of IB1	Grams of LAS	Meq of LAS	Total meq/g of Mixture
1.0	2.20	0.0	0.00	2.20
0.9	1.98	0.1	0.29	2.27
0.8	1.76	0.2	0.57	2.33
0.7	1.54	0.3	0.86	2.40
0.6	1.32	0.4	1.15	2.47
0.5	1.10	0.5	1.44	2.54
0.4	0.88	0.6	1.72	2.60
0.3	0.66	0.7	2.01	2.67
0.2	0.44	0.8	2.30	2.74
0.1	0.22	0.9	2.59	2.81
0.0	0.00	1.0	2.87	2.87

The disparate aromatic multiplets in PMR Spectrum No. 3 (464 and 423 Hz) again indicate sulfonation of the aromatic nucleus. The area of absorption centered at 196 Hz is attributed to the combination of signals from the sulfonamido methylene ($-SO_2NHC\underline{H}_2-$) and sulfonato methylene ($-C\underline{H}_2SO_3Na$) protons. These signals should integrate to four protons if the material were pure. The fact that this area represents only three protons, with respect to the overall spectrum, leads to the conclusion

SPECTRUM NO. 3
SAMPLE
SOLVENT
TEMPERATURE
FILTER BANDWIDTH
R.F. FIELD
SWEEP TIME
SWEEP WIDTH
SWEEP OFFSET
SPECTRUM AMP.
INTEGRAL AMP.
REMARKS
A
B
4.0
2.0
250
250
500
500
0
5.0
20.0
°C
TMS
74
53
194
130
444
433
CHART
PPM (δ)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

that the product contains 75% of the desired surfactant, IB1, which is less than that indicated by the anion determination.

Surfactant IB2: Sodium N-methyl-dodecylbenzenesulfonamidoethylsulfonate ($C_{12}H_{25}C_6H_4SO_2N(CH_3)CH_2CH_2SO_3Na$)

$$C_{12}H_{25}C_6H_5 \xrightarrow{2ClSO_3H} C_{12}H_{25}SO_2Cl \xrightarrow[\text{Base}]{NH(CH_3)CH_2CH_2SO_3H}$$

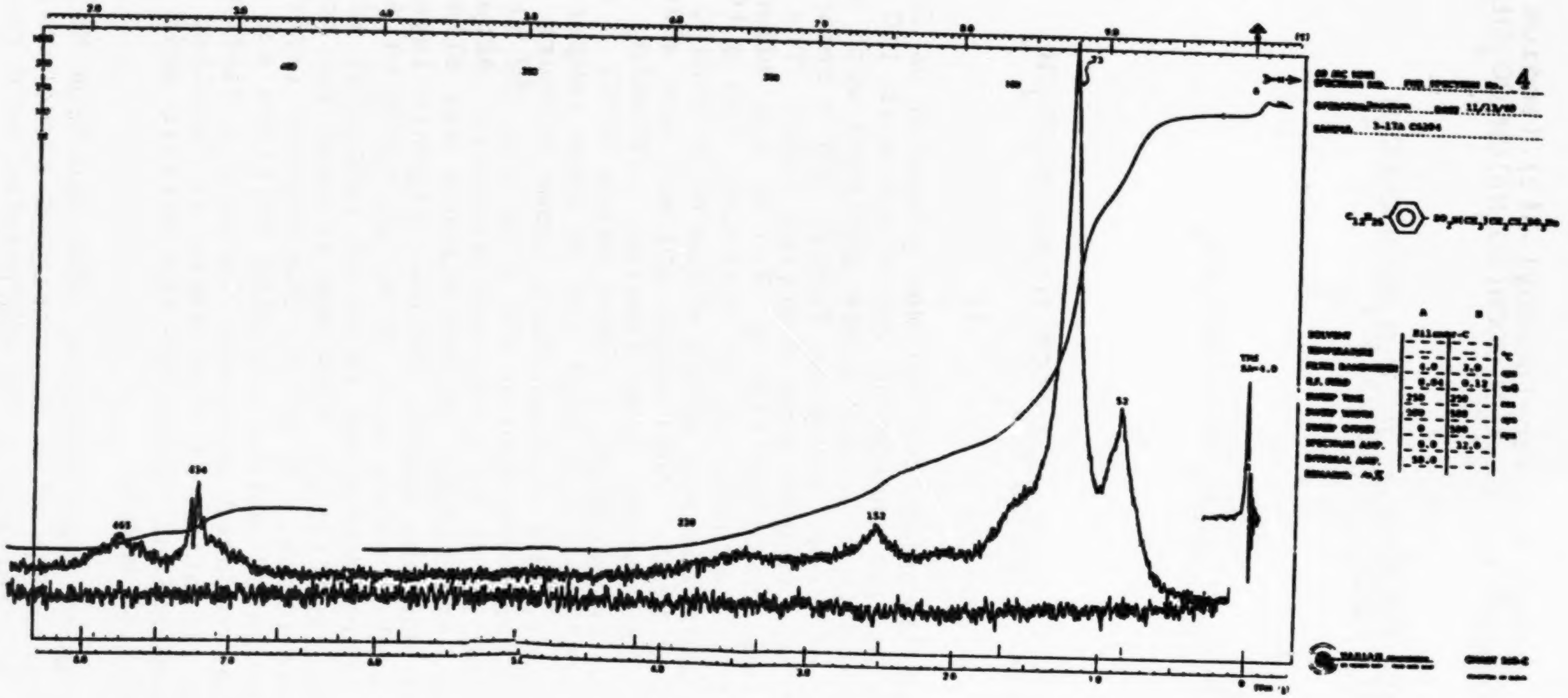
$$C_{12}H_{25}SO_2N(CH_3)CH_2CH_2SO_3Na$$

The solution of dodecylbenzenesulfonyl chloride (0.4 m) was slowly added, at room temperature, to a mixture containing 198.4 g of 65% aqueous sodium N-methyltaurate (equivalent to 0.8 m N-methyltaurine, sodium salt), 130 g of sodium bicarbonate and 175 ml of water. During the course of this addition 75 ml of dichloroethane and 100 ml of water were added to maintain the fluidity of the mixture so that magnetic stirring was effective. (No additional sodium bicarbonate was required to maintain the basicity of the reaction mixture.) After the addition, the reaction mixture was heated with a hot water bath for 2 hours with occasional stirring. The mixture was then heated to a boil and 150 ml of isopropyl alcohol was added. After cooling in a separatory funnel, the lower aqueous layer was separated; the upper organic layer was stripped of solvent under reduced pressure and the residue was dried in a vacuum oven at 50-60°C/13 torr. The pale yellow solid was extracted with 350 ml of hot methanol yielding 125 g of material after removal of the methanol and drying. Because the anion determination of this material was an unsatisfactory 1.91 meq/g, the product was then extracted with hot absolute ethanol. After removal of the solvent and drying, the anion titre was 2.10 meq/g which is slightly lower than the theoretical of 2.13 shown in the following Table.

CALCULATED CATIONIC TITRATION VALUES FOR MIXTURES OF SODIUM N-METHYL-DODECYLBENZENESULFONAMIDOETHYLSULFONATE (IB2) AND SODIUM DODECYLBENZENESULFONATE (LAS)

Grams of IB2	Meq of IB2	Grams of LAS	Meq of LAS	Total meq/g of Mixture
1.0	2.13	0.0	0.00	2.13
0.9	1.92	0.1	0.29	2.21
0.8	1.70	0.2	0.57	2.27
0.7	1.49	0.3	0.86	2.35
0.6	1.28	0.4	1.15	2.43
0.5	1.06	0.5	1.44	2.50
0.4	0.85	0.6	1.72	2.57
0.3	0.64	0.7	2.01	2.65
0.2	0.43	0.8	2.30	2.73
0.1	0.21	0.9	2.59	2.80
0.0	0.00	1.0	2.87	2.87

The PMR spectrum of this material (No. 4) did not corroborate this high purity. There is a significant signal at 434 Hz which is superposed on a portion of the sulfonated alkylbenzene proton signals. This indicates the presence of some unreacted dodecylbenzene. Consideration of the integration in this region gives an 85% purity. However, the integration ratio between the remaining signal areas (132-230 Hz vs 40-120 Hz) substantiates only an 80% purity. This material was used in formulation work but did not show promise and was dropped as a candidate surfactant.


4
11/13/80
TMS
73
52
152
230
634
665
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
A
B
1.0
2.0
0.04
0.12
250
250
500
500
0
500
8.0
32.0
50.0

Surfactant II: Methyl 3-dodecylbenzoyl-3(2)-(sodium sulfonato)propionate[8] ($C_{12}H_{25}C_6H_4COCH(SO_3Na)CH_2CO_2CH_3$)

$$C_{12}H_{25}C_6H_5 \xrightarrow[\text{Anhyd. AlCl}_3]{\text{Maleic Anhyd.}} C_{12}H_{25}C_6H_4COCH{=}CHCO_2H$$

a b

$$\xrightarrow[\text{Dichloroethane}]{CH_3OH/H^+ \text{ Reflux}} C_{12}H_{25}C_6H_4COCH{=}CHCO_2CH_3$$

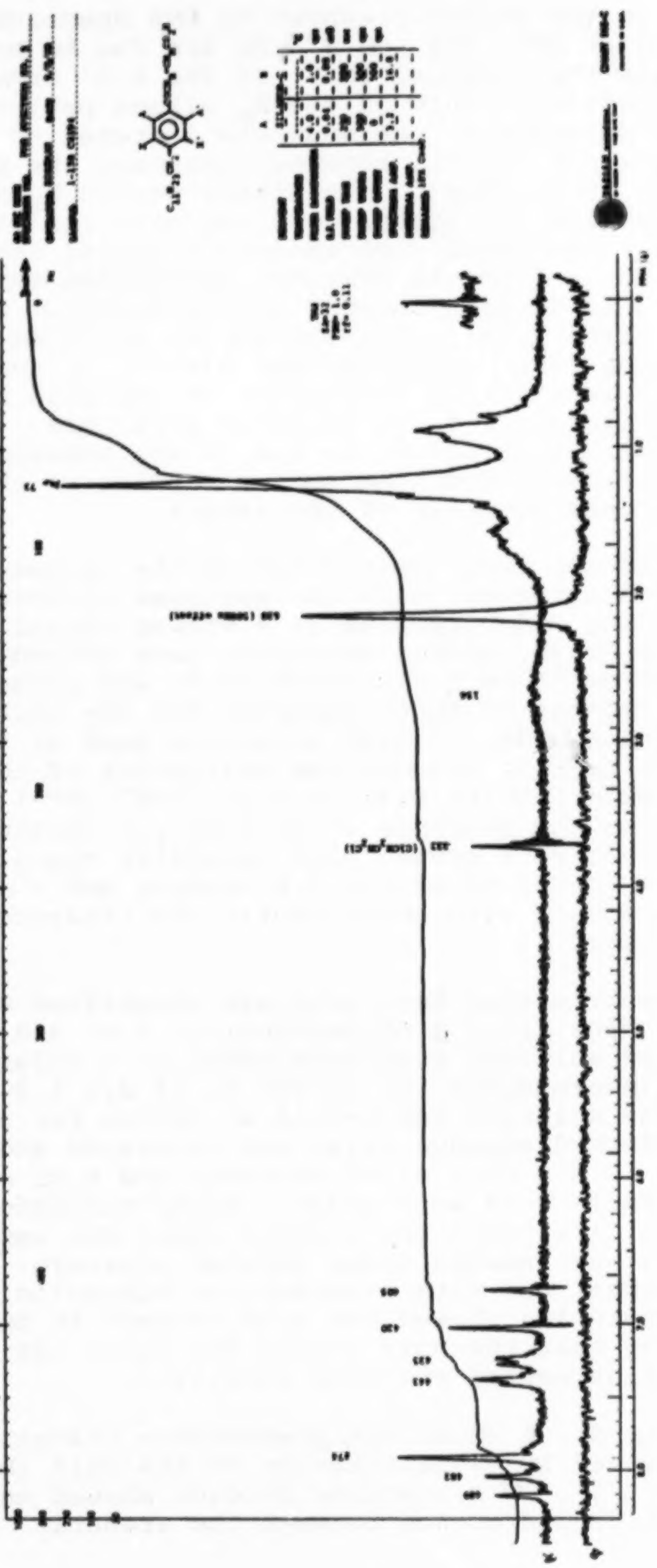
c

$$\xrightarrow[110\text{-}140°/\text{Pressure}]{NaHSO_3} C_{12}H_{25}C_6H_4COCH(SO_3Na)CH_2CO_2CH_3$$

II

The acrylic acid intermediate (b) was prepared as follows: 44 g (0.5 m) of maleic anhydride was mixed with 110 g of dry dichloroethane in a 3-neck flask equipped with a thermometer, magnetic stirrer, dropping funnel and a reflux condenser which was topped with a drying tube. The anhydrous aluminum chloride (105 g, 0.8 m) was added with cooling and, after ten minutes of stirring, 123 g (0.5 m) of dried dodecylbenzene was added while maintaining the temperature below 15°C. Additional solvent was added as needed to keep the mixture free flowing. (Foaming is minimized if the temperature is held below 11°C). After stirring at 10-15°C for 1/2 hour and at room temperature for 3/4 of an hour, the viscous dark brown mixture was poured into a beaker containing 450 g of ice, 50 ml of 66% sulfuric acid and 15 ml of isopropyl alcohol. After thorough mixing, the bright yellow mixture was allowed to stand overnight and the upper, yellow, organic layer was separated and washed twice with 70 ml portions of 66% sulfuric acid which contained 10 ml of isopropyl alcohol, making sure that sufficient time was allowed for complete layering to take place. Finally, the organic layer was washed with saturated sodium chloride solution and stripped of solvent under reduced pressure, leaving a viscous amber liquid. Basic titration of this material required 2.54 meq/g. The theoretical value for the acrylic acid intermediate (b) is 2.69 meq/g.

The PMR spectrum of this material (PMR Spectrum No. 5) is in excellent agreement with the assigned structure. The signal at 628 Hz represents the carboxylic acid proton while the signals between 400 and 500 Hz are the aromatic and alkene protons. Expansion of this region (not shown) and consideration of the effects of esterification in the next step lead to the following specific assignments with

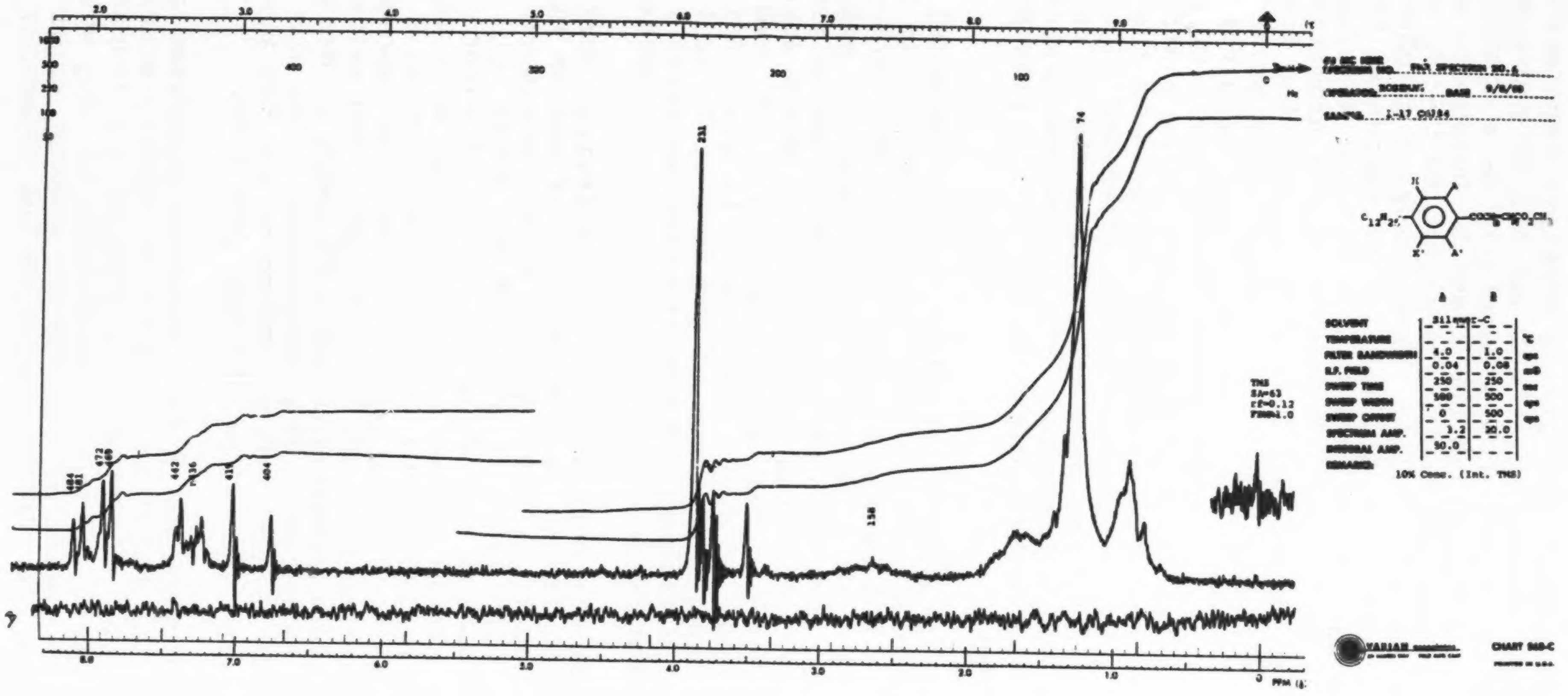


reference to the structure shown on PMR Spectrum No. 5: The signals at 489, 482 and 474 Hz are due to protons A,A' and H_M where the chemical shift of the A,A' aromatic protons is close to that of the H_M alkene proton causing overlap of multiplets; the doublets centered at 443 and 435 Hz represent the XX' aromatic protons; the peaks at 420 and 405 Hz are due to the alkene proton H_B which shows as a doublet due to (trans) coupling with its vinylic neighbor H_M; the broad, low intensity signal centered at about 162 Hz is from the somewhat deshielded methylene group which is directly bonded to the aromatic nucleus; the broad based, high intensity signal at 73 Hz is due to the remaining alkyl (hydrocarbon) portion of the molecule. The overall integration (exclusive of the acid proton) is quite satisfactory for the assigned structure. The sharp signal appearing at 223 Hz is due to the presence of residual 1,2-dichloroethane and, according to the integration, comprises about 4% of the sample.

The infrared spectrum (neat film) of the washed product was also in good agreement with the assigned structure. The C-H stretching mode appeared as a strong signal (ca. 3.5μ) with a very broad, medium intensity base extending from 2.85μ (3500 cm^{-1}) to 4.17μ (2400 cm^{-1}) and possessed maxima which are typical of those expected for the carboxylic acid O-H stretching mode. A high intensity peak at 5.85μ (1709 cm^{-1}) readily assumes the assignment of the acid carbonyl (dimer) while that at 6.0μ (1667 cm^{-1}) can be correlated to the presence of an aryl α,β-unsaturated ketone. Finally, a broad, high intensity signal at 7.75μ (1290 cm^{-1}) (coupling of the O-H bending and -C-OH stretching modes) also corroborates the presence of a carboxylic acid.

Next, the unsaturated keto acid was esterified with methanol. Thus, 19.2 g of methanol (0.6 m) and 10 ml of concentrated sulfuric acid were added to a solution of the above dry intermediate (b) in 100 ml of dry 1,2-dichloroethane. The solution was heated at reflux for 3/4 of an hour, the formed aqueous layer was separated and an additional 12.8 g (0.4 m) of methanol and 6 ml of concentrated sulfuric acid were added. After refluxing for an additional 1 1/2 hours the organic layer was separated and the solvent was removed under reduced pressure. Titration of the residual oil with standardized ethanolic potassium hydroxide solution showed the acid content to be less than 4% (assuming that the only source for titre was from the presence of unreacted starting material).

PMR Spectrum No. 6 shows the predictable changes which would be caused by esterification of the acid (PMR Spectrum No. 5). The reaction product showed an increased chemical shift difference between the aromatic "A" protons


2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
400
300
200
100
0
Hz
74
231
158
484
481
472
469
462
436
419
404
TMS
SA=63
rf=0.12
FSW=1.0
SPECTRUM NO. 6
OPERATOR DATE 9/8/80
SAMPLE 1-17 CHU84
$C_{12}H_{25}O$
X
A
X'
A'
A
B
SOLVENT
Silanor-C
TEMPERATURE
FILTER BANDWIDTH 4.0 1.0
R.F. FIELD 0.04 0.08
SWEEP TIME 250 250
SWEEP WIDTH 500 500
SWEEP OFFSET 0 500
SPECTRUM AMP. 3.2 30.0
INTEGRAL AMP. 30.0
REMARKS
10% Conc. (Int. TMS)
VARIAN
CHART 360-C
PRINTED IN U.S.A.
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)

and the vinyl proton, H_M, giving complete separation of these signals. The peaks at 481 and 472 Hz represent the A and A' protons which show essentially as a doublet due to the ortho coupling with the X and X' neighbors while the absorptions at 484 and 469 are assigned to the H_B vinylic proton which is split by its (trans)vinylic neighbor, H_M. The signals centered at 442 and 436 Hz represent the aromatic "X" protons and the singlets at 419 and 404 represent the remaining H_M proton. Expansion of the aromatic and alkene signals showed the following correlating coupling constants: $JH_{AX(A'X')} = 8.4$ Hz, $JH_{BM} = 15.5$ Hz and $JH_{XX'} = 1.8$ Hz while $JH_{AA'}$ and $JH_{AX'(A'X)}$ were not resolvable. The carboxylic acid proton absorption ($-CO_2\underline{H}$) of the starting material is no longer present while a strong signal at 231 Hz now appears which is assigned as the carbomethoxy ($-CO_2C\underline{H}_3$) protons. The low intensity signals just upfield of this latter peak are probably due to residual methanol and dichloroethane. The signal immediately adjacent to the methoxy might be due to the presence of some *cis* isomer.

The infrared spectrum (neat film) of this material showed an almost complete loss of the broad, strong acid O-H absorption in the region of 2.85-4.17μ. The carbonyl stretching peak at 5.75μ (1739 cm^{-1}) shows the expected shift for the formation of an ester while esterification had little effect on the ketone carbonyl which appears at 5.95μ (1681 cm^{-1}). The appearance of a broad, medium intensity signal at 8.55μ (1170 cm^{-1}) is also indicative of an ester when correlated to the band at 7.75μ (1290 cm^{-1}) which was also present for the starting material (symmetrical and asymmetrical stretching of C-O-C, respectively).

Conversion of the acrylate (*c*) to the desired surfactant (*II*) was accomplished by the addition of sodium bisulfite across the double bond (Step 3). A Parr pressure reactor was charged with 140 g (0.39 m) of the ester (*c*), 40.5 g (0.39 m) of sodium bisulfite and 140 ml of water. The mixture was heated in the sealed container with stirring for 3 hours at 110-140°C; the pressure reaching a maximum of 60 lbs at 140°C. The yellow mixture was removed and dried in a vacuum oven at 55°C/13 torr. The anion content of this particular material was 1.99 meq/g as determined by cationic titration. The theoretical value for surfactant II is 2.16 meq/g, inferring ca. 90% purity. (All other runs gave values higher than 1.99).

The infrared spectrum of this material possessed a strong signal at 9.52μ (1050 cm^{-1}) which is readily attributed to the symmetrical $-SO_2$ stretching mode of a sulfonate group. The accompanying asymmetric stretching of $-SO_2$ would appear in the region of the already present ester C-O-C stretching region. Additionally, a low intensity signal which was present for the starting acrylate (c) at 6.1μ (1639 cm^{-1}) was no longer present in the bisulfite addition product. The loss of this signal would be expected if it were due to the -C=C- stretching mode of the alkene functional group.

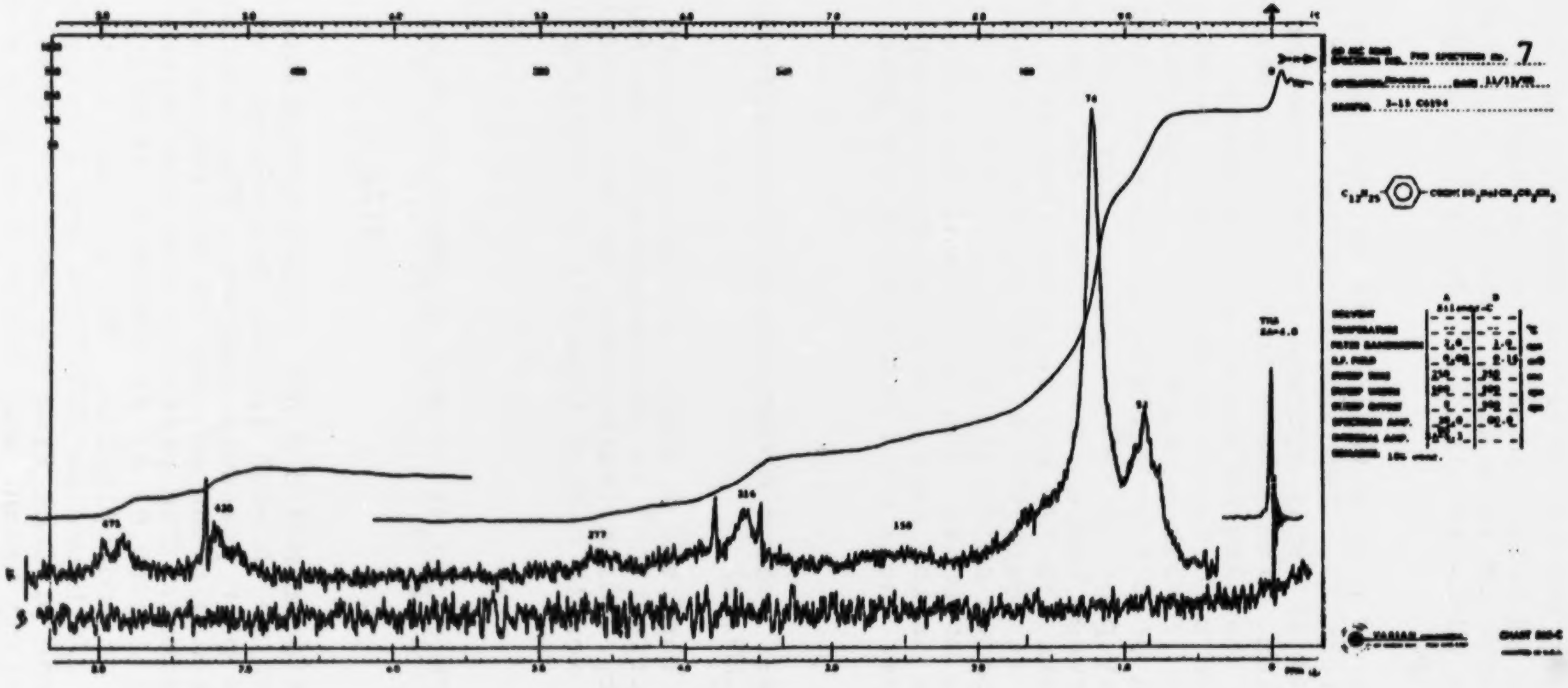
PMR Spectrum No. 7 pretty well verifies the general structure of surfactant II. Two well-separated, broad multiplets represent the AA'XX' spin systems for the expected aromatic para substitution. The alkene proton signals which were present in the starting material are now absent. The low intensity, broad band centered at 277 Hz is readily assigned as the sodium sulfonato methine proton ($-C\underline{H}SO_3Na$) while the absorption band at 216 Hz represents the ester methylene and carbomethoxy protons ($-C\underline{H}_2CO_2C\underline{H}_3$). The ratio of the integration between these latter signals and the remaining hydrocarbon peaks (30-170 Hz) verifies that this material should contain at least 80% of the desired surfactant II. Although the sodium sulfonato group is shown in a specific location in the molecule, the analytical data does not prove that this is the case. The sulfonato group can in fact be in either the 2 or 3 position of the propionate nucleus.

Surfactant IIIA: Sodium dodecylaminoethanesulfonate ($C_{12}H_{25}NHCH_2CH_2SO_3Na$)

The literature reported a simple procedure for the preparation of this surfactant[9] in accordance with the following reaction whereby sodium isethionate (b) and dodecylamine (a) were merely heated together at atmospheric pressure.

$$\begin{array}{ccccc} C_{12}H_{25}NH_2 & + & HOCH_2CH_2SO_3Na & \longrightarrow & C_{12}H_{25}NHCH_2CH_2SO_3Na \\ \underline{a} & & \underline{b} & & \text{IIIA} \end{array}$$

In our case, this method did not supply acceptable material and, rather than go through lengthy procedures, we resorted to the use of a parr pressure reactor. The reaction is best accomplished without solvent in accordance with the following procedure: The pressure reaction vessel was charged with 12.2 g (0.82 m) of sodium isethionate and 158.6 g (0.86) of dodecylamine. The mix was heated with stirring for 3 1/2 hours at 200-225°C and 2 hours at 245-265°C. The crude product from the reaction vessel was washed with boiling hexane and, after drying in a vacuum oven, the solid was extracted with boiling absolute methanol. Removal of the solvent under reduced pressure, followed by drying in a vacuum oven at 70°C/13 torr,


7
3-15 C6194
TMS
74
9
150
216
277
430
475
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
ppm
10% conc.
VARIAN

yielded a pale yellow powder which melted at 275-280°C, showing decomposition at 175°C. Since this material is amphoteric (possessing the amino and sulfonate functions), cationic titration is of little value for estimating the purity of this species.

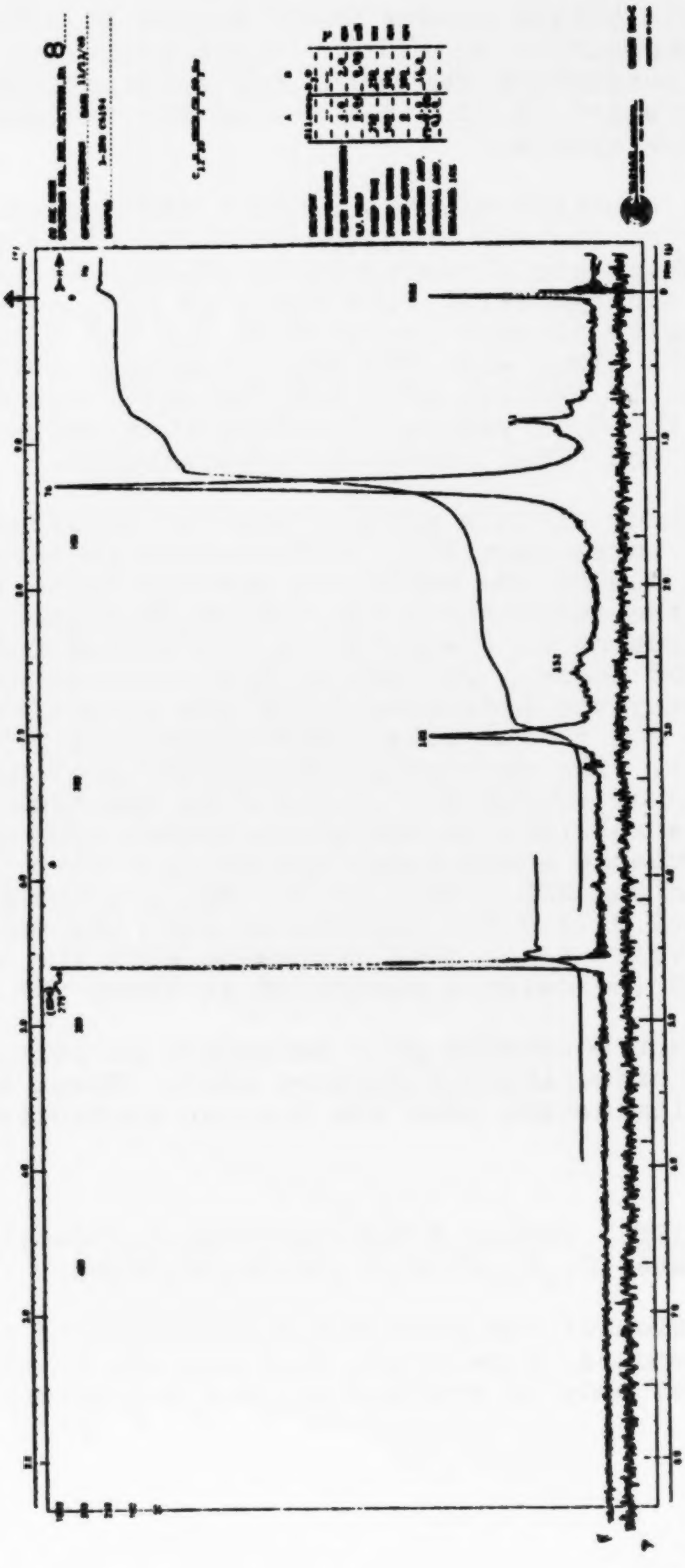
The infrared spectrum of this product (KBr pellet) exhibits strong signals at 8.45 and 9.35μ (1183 and 1070 cm-1) which are characteristic of the sulfonate group (asymmetric and symmetric stretching of $-SO_2$ respectively). Medium intensity signals centered at 3.5 and 6.85μ (2857 and 1460 cm-1) along with the low intensity, broad group of bands between 12 and 14μ (833 and 714 cm-1) are due to the presence of the C_{12} hydrocarbon chain (C-H stretching, $-CH_2$ bending and $(CH_2)_n$ rocking respectively).

The PMR spectrum of this product (No. 8) verifies the structure of surfactant IIIA. The medium intensity signal at 181 Hz is due to the methylene protons which are alpha and beta to the sulfonato group ($-N-C\underline{H}_2C\underline{H}_2SO_3Na$) where the amino substitution on the $\underline{\beta}$ carbon has caused sufficient deshielding of these $\underline{\beta}$ protons to give overlap with the α sulfonato methylene hydrogens. The low intensity multiplet at 152 Hz is due to the alkyl amino methylene protons ($C_{11}H_{13}C\underline{H}_2N-$). The remaining hydrocarbon protons appear in the region of 40-115 Hz. Since this spectrum was recorded as a solution in deuterium oxide, hydrogen-deuterium exchange would cause the amino proton (-NH) to appear within the HDO signal at 275 Hz. An integration ratio of 4.4:2.0:23.0 for signals at 181, 152 and 120-40 Hz, respectively, is in good agreement with the assigned structure and indicates a purity of at least 90%.

This surfactant possessed poor detergent properties and possessed an objectionable pungent odor. These drawbacks forced its elimination from the list of candidate surfactants.

Surfactant IIIB: Sodium N-hydroxyethyl-2-dodecylaminoethanesulfonate ($C_{12}H_{25}N(CH_2CH_2OH)CH_2CH_2SO_3Na$)

In consideration of the poor characteristics of the preceding compound, from which this one was to be prepared, no attempt was made to synthesize this surfactant (IIIB).


8

Surfactant IVA: Dodecyl 3-(sodium levulinate) sulfone ($C_{12}H_{25}SO_2CH(COCH_3)CH_2CO_2Na$)

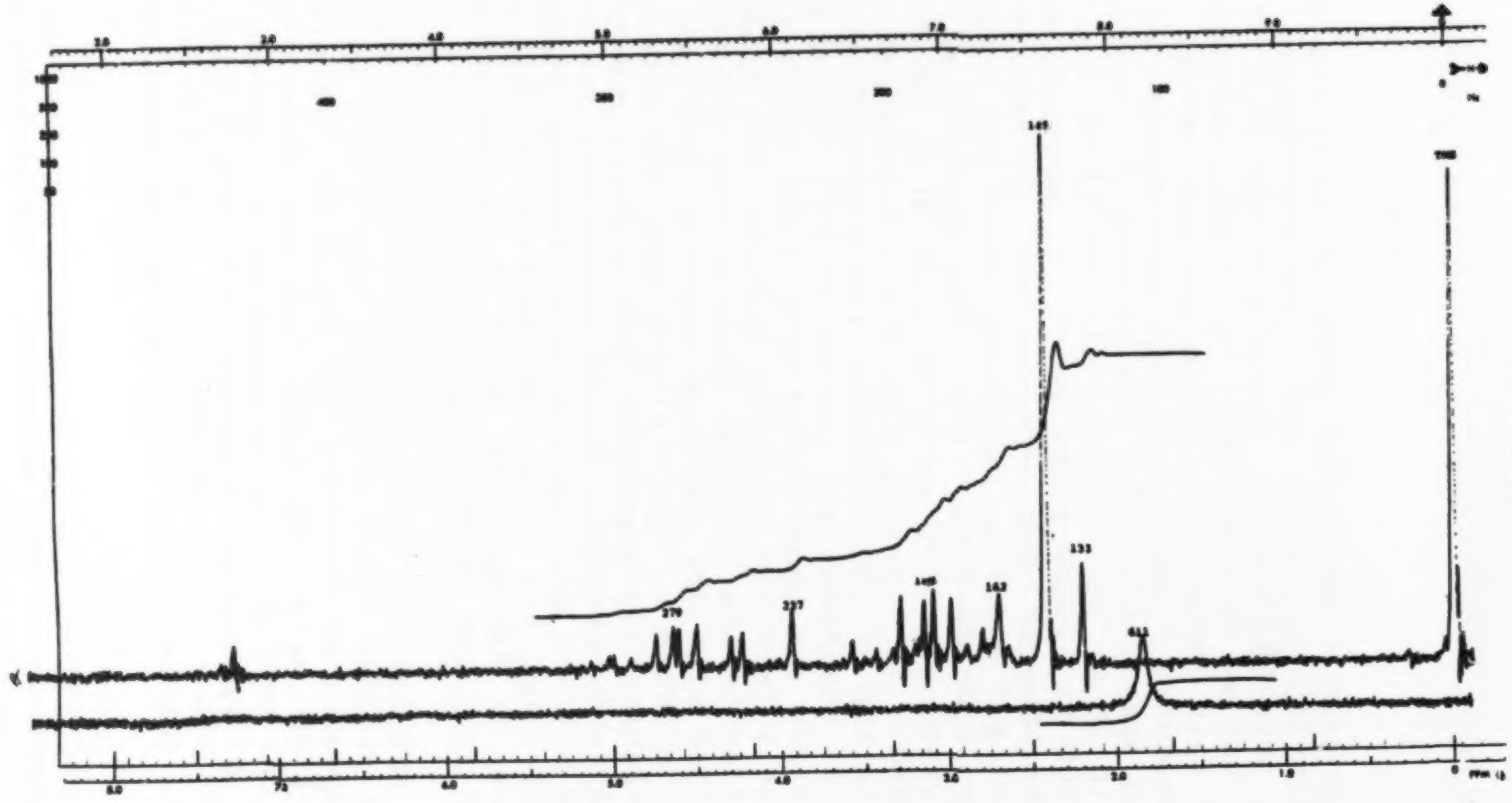
$$\underset{\underline{a}}{CH_3COCH_2CH_2CO_2H} \xrightarrow{Br_2} \underset{\underline{b}}{CH_3COCHBrCH_2CO_2H} \xrightarrow{RS^-Na^+}$$

$$\underset{\underline{c}}{CH_3COCH(SR)CH_2CO_2Na} \xrightarrow{\text{Oxidation}} \underset{\text{IVA}}{CH_3COCH(SO_2R)CH_2CO_2Na}$$

In our work we used a commercial grade of levulinic acid (a) as the starting material. Our first experiments in preparing the intermediate, b, duplicated the work of Hurd and Ferraro[10] but we were not able to isolate sufficient quantities of this material (3-bromolevulinic acid). The following procedure, however, yielded good amounts of crude material which was suitable for use in Step 2. Levulinic acid, 32.5 g (0.28 m) was dissolved in 175 ml of dry benzene in a 500 ml 3-neck flask which was equipped with an internal thermometer, magnetic stirrer, gas equilibrating dropping funnel and a reflux condenser which was topped with a hydrogen bromide water trap. The solution was heated to, and maintained at, 65°C while 45 g (0.28 m) of bromine was slowly added with stirring over a 1 1/4-hour period. The trap at the top of the condenser was replaced by a drierite tube as the flask was cooled to room temperature. The reaction flask was then fitted with a gas inlet tube which dipped well into the reaction mixture, the drierite tube was replaced by the hydrogen bromide trap and the system was purged with dry nitrogen until no hydrogen bromide was detectable in the effluent from the outlet tube. The benzene solution was separated from a small amount of dark brown, benzene insoluble liquid (which was not investigated) and the solvent was removed under reduced pressure, leaving 53 g of amber oil. The PMR spectrum of this crude product is shown in PMR Spectrum No. 9 while that of the levulinic acid is given in PMR Spectrum No. 10.

Although Hurd and Ferraro[10] found that bromination of levulinic acid yielded the 3,5-dibromo derivative as well as 3-bromo compound, no evidence was found for the presence of 5-bromolevulinic acid. We found that the crude product isolated from our procedure of bromination in benzene is of the following approximate composition: 64% 3-bromolevulinic acid; 13% 3,5-dibromolevulinic acid; 13% 5-bromolevulinic acid; 10% levulinic acid (unreacted starting material).

The above composition of the crude product was determined from the PMR spectrum of this material. The structures and proton designations follow.



60 MC NMR
SPECTRUM NO. PMR SPECTRUM No. 9

OPERATOR [illegible] DATE 2/11/78

SAMPLE 4-16 CN194

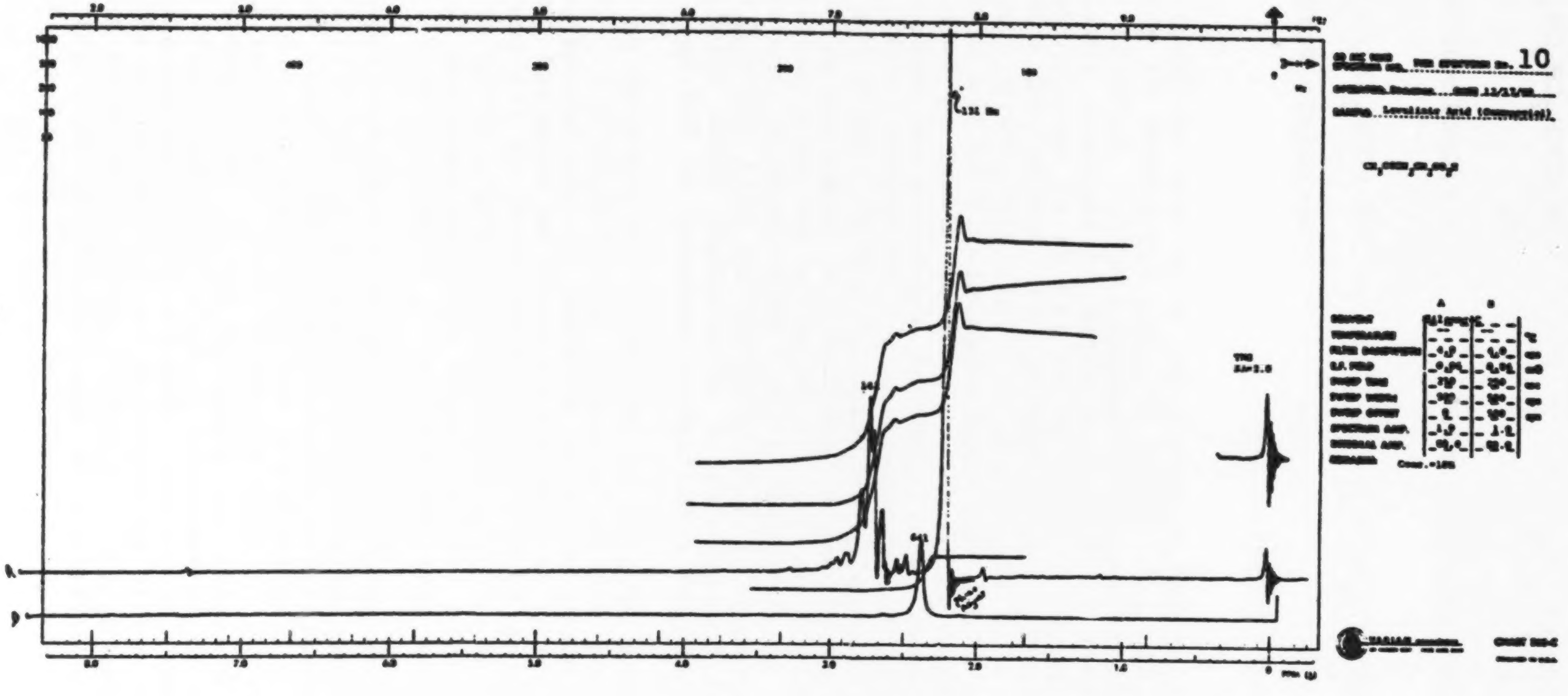
Crude Product from
Bromination of Levulinic
Acid in Benzene

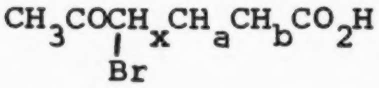
	A	B	
SOLVENT	Silanor-C		
TEMPERATURE	--	--	°C
FILTER BANDWIDTH	4.0	4.0	cps
R.F. FIELD	0.04	0.04	mG
SWEEP TIME	250	250	sec
SWEEP WIDTH	500	500	cps
SWEEP OFFSET	0	500	cps
SPECTRUM AMP.	5.0	5.0	
INTEGRAL AMP.	80.0	80.0	
REMARKS	(rf=0.12)		

Approximate Composition:
3-bromolevulinic Acid-64%
5-bromolevulinic Acid-13%
3,5-dibromolevulinic Acid-13%
levulinic Acid-10%

VARIAN

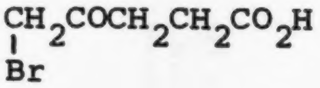
CHART 100-C


10
Levulinic Acid (Commercial)
TMS
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM (δ)



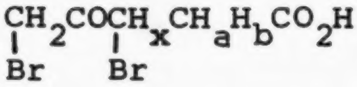
$$CH_3COCH_xCH_aCH_bCO_2H \quad (3\text{-}Br)$$

3-Bromolevulinic Acid



$$CH_2COCH_2CH_2CO_2H \quad (5\text{-}Br)$$

5-Bromolevulinic Acid



$$CH_2COCH_xCH_aH_bCO_2H \quad (3,5\text{-}Br_2)$$

3,5-Dibromolevulinic Acid

$CH_3COCH_2CH_2CO_2H$

Levulinic Acid

Comparison of PMR Spectrum No. 9 to that of levulinic acid (Spectrum No. 10) allows for the assignment of the 133 and 162 Hz signals as the respective methyl carbonyl ($C\underline{H}_3CO-$) and methylene ($-C\underline{H}_2C\underline{H}_2-$) protons of residual levulinic acid. The high intensity signlet at 145 Hz is best interpreted as the slightly deshielded methyl carbonyl of 3-bromolevulinic acid ($C\underline{H}_3COCHBr-$). This assignment comes from the expectation that the electronegativity of the bromine at this position would show a minimal amount of deshielding of these carbonyl methyl protons which are two carbons removed. The correlating bromomethine proton signal ($-COC\underline{H}_xBr-$) is seen as a multiplet centered at 279 Hz, where the effects of direct bromination deshield the remaining proton ($-H_x$) very greatly from the 162 Hz value for this position methylene in levulinic acid. Additionally, the methylene-carboxy protons of 3-bromolevulinic acid ($C-C\underline{H}_a\underline{H}_bCO_2H$) would feel the effects of an adjacent bromo substitution and are found as a multiplet centered at 188 Hz.

The apparent singlet at 237 Hz is interpreted as the bromomethylene of 5-bromolevulinic acid (CH_2BrCO-). The methylene group which is adjacent to the ketone group ($-COC\underline{H}_2-C-$) in this molecule would be expected somewhat downfield (ca 10 Hz) from 162 Hz which is its position in levulinic acid. The remaining methylene group of 5-bromolevulinic acid ($-C-C\underline{H}_2-CO_2H$) would be expected to appear at about the same position as in levulinic acid.

The presence of a small amount of 3,5-dibromolevulinic acid in this crude material is indicated by the very low intensity multiplet centered at 300 Hz. These signals are assigned as representing the 3-bromomethine proton ($-COC\underline{H}_xBr-C-$) of this molecule where additional bromination at the 5 position has supplied enough of a deshielding effect so as to separate it from the same signal of the 3-monobromo derivative. The carboxymethylene signals ($-C\underline{H}_2CO_2H$) would be expected in the region of 188 Hz while the bromomethylene ($C\underline{H}_2BrCO-$) protons would be expected somewhat downfield from the 5-monobromo derivative. Thus, the apparent doublet centered at 257 Hz answers this final expectation. The anomaly that this latter assignment is a doublet rather than an expected singlet might be rationalized on the basis of restricted rotation about the carbonyl carbon caused by 3,5-dibromo substitution. The carboxylic acid protons for all species appear at 611 Hz.

There are four signal areas in the PMR spectrum of the crude product which, individually, represent one of each of the components of the mixture. Furthermore, the regions are separated enough so that their integrations can be used to determine an approximate composition. The signal areas involved are those at: (1) 300 Hz, representing the bromomethine ($-COC\underline{H}_xBr-C$) of 3,5-dibromolevulinic acid, (2) 279 Hz, representing the bromomethine ($-COC\underline{H}_xBr-C$) of 3-bromolevulinic acid (the carbonylmethyl of this species at 145 Hz is also separated well enough to be used for this purpose and corroborates the analysis which uses the signal at 279 Hz), (3) 237 Hz, representing the bromomethylene (CH_2BrCO-) of 5-bromolevulinic acid, and (4) 133 Hz, representing the methyl carbonyl ($C\underline{H}_3CO-$) of levulinic acid. Equalizing the integrations with respect to the number of protons involved in the signal regions and calculating their ratios yielded the composition given above.

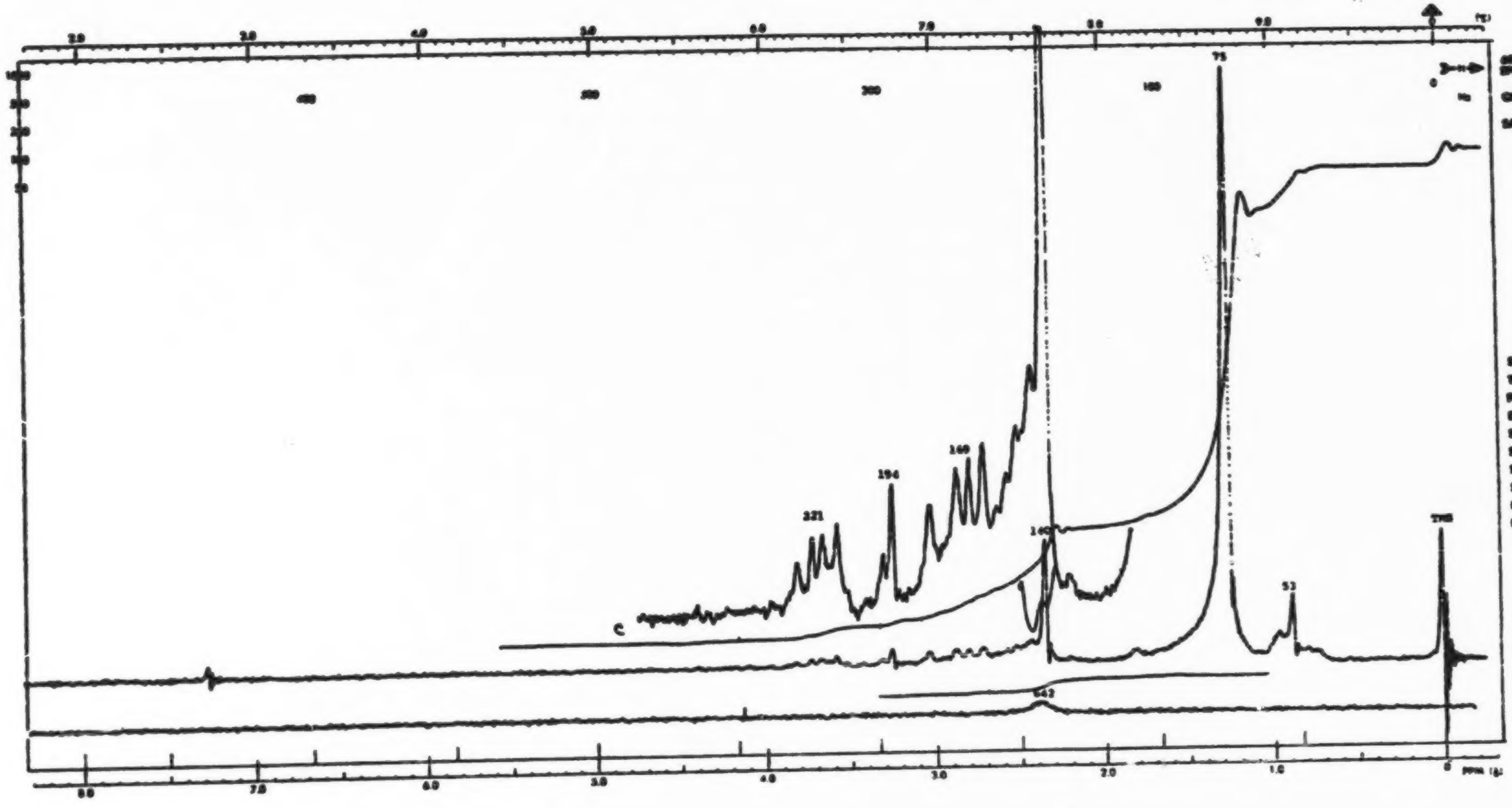
Because distillation caused significant decomposition of the products and further attempts to purify this material (e.g., crystallization) were unsuccessful, we chose to use this material as is for the next step of the synthesis. This, of course, was done with the hope that purification of the next intermediate would be easier to accomplish.

In this next step, 15.8 g of potassium hydroxide was dissolved in 50 ml of absolute ethanol in a flask which was equipped with a magnetic stirrer, internal thermometer, gas equilibrating dropping funnel and a reflux condenser which was topped with a drierite tube. n-Dodecylmercaptan, 20.2 g (0.1 m), was added to the ethanolic KOH solution and, after 1 minute of stirring, 24.4 g of the crude brominated acid product was added over a period of 1.25 hours. The addition was done in such a manner so as to maintain a 31-32°C internal temperature range. The precipitated potassium bromide was filtered and the clear filtrate was stripped of solvent at reduced pressure. The residue (36.6 g) was dissolved in 200 ml of water and the solution was acidified with concentrated HCl (6 ml) to a pH of 3 (pHydrion paper) while cooling in an ice bath. The precipitate was filtered, pressed dry in the filter, allowed to air dry and then placed in a vacuum oven at 50°C/10 torr. Upon cooling to room temperature the residual oil solidified yielding 33 g of waxy, low melting, tan solid. This material was very soluble in all common organic solvents but was recrystallized from an acetone-water solvent system. The PMR and IR spectra of the recrystallized material were virtually the same as the crude product.

PMR Spectrum No. 11 is that of the crude product obtained from treatment of the bromo acids with potassium n-dodecylmercaptide and leaves no doubt that the mercaptide effectively displaced the bromo groups of the brominated levulinic acids to give a mixture of thioethers. The loss of all signals downfield of 221 Hz (except the acid proton at 642 Hz) indicates that no bromo acids were present in this material. The work-up for this reaction apparently eliminated the presence of unreacted levulinic acid since there is no appreciable absorption in the region of 131 Hz where the methyl carbonyl ($C\underline{H}_3CO-$) of levulinic acid would appear. Because sulfur substitution has less of an electronegative effect than bromine, the signals are not separated as much as those of the bromo derivatives. Even so, interpretation of the data leads us to conclude that this material is a mixture consisting of about 80% of the desired n-dodecyl 3-levulinic acid sulfide (c) and 20% n-dodecyl 5-levulinic acid sulfide ($C_{12}H_{25}SCH_2COCH_2CH_2CO_2H$).

The signals centered around 221 Hz represent the thiomethine proton ($-COC\underline{H}S-$) of the 3-bromo compound while the signal at 194 Hz would represent the thiomethylene protons ($-SC\underline{H}_2CO$) of the 5-bromo acid. The sharp signal at 140 Hz represents the carbonylmethyl group ($C\underline{H}_3CO-$) of the 3-substituted levulinic acid (c). This signal overlaps in the area of absorption for a methylene group which is directly bonded to sulfur ($-C\underline{H}_2S-$). The source of these latter signals would, of course, be from the n-dodecyl chain ($C_{11}H_{23}-C\underline{H}_2S-$). The high intensity signal at 75 Hz is from the hydrocarbon chain methylene ($-C\underline{H}_2$) groups while the small signal area at 53 Hz is due to terminal hydrocarbon methyl protons (CH_3-C-). The infrared spectrum of the crude sulfide confirmed the presence of the carboxylic acid and ketone functional groups.

A number of attempts were made to oxidize the mixture of thioethers to their desired sulfone derivatives. None of these experiments were successful in supplying the desired surfactant IVA. Therefore, the value of this type of surfactant in phosphate-free formulations was not investigated.



60 MC PROBE
SPECTRUM NO. NMR SPECTRUM No. 11

OPERATOR FORDYCE DATE 3/26/70

SAMPLE 6-30b C6194

Crude reaction product of
the bromo acid with
potassium mercaptide

	A	B		C
SOLVENT	CCl_4			
TEMPERATURE	--	--	°C	--
FILTER BANDWIDTH	4.0	4.0	cps	1.0
R.F. FIELD	0.06	0.06	mG	.16
SWEEP TIME	250	250	sec	250
SWEEP WIDTH	500	500	cps	500
SWEEP OFFSET	0	500	cps	0
SPECTRUM AMP.	2.5	2.5		32.0
INTEGRAL AMP.	80.0	80.0		--

REMARKS 5% concentration

Mixture:

$CH_3COCH(SC_{12}H_{25})CH_2CO_2H$
$CH_2(SC_{12}H_{25})COCH_2CH_2CO_2H$

VARIAN

CHART 360-C

1 Accession Number

2 Subject Field & Group
05G

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5 Organization
IIT Research Institute, Chicago, Illinois

6 Title
DEVELOPMENT OF PHOSPHATE-FREE HOME LAUNDRY DETERGENTS

10 Author(s)
Roseman, Karl A.
Linfield, Warner M.

16 Project Designation
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25 Identifiers (Starred First)
Phosphate-free detergents*

27 Abstract

Basic studies were performed towards the development of phosphate-free home laundry detergents. Five surfactants were synthesized with the idea that they might possess hard ion chelating properties. The cleaning abilities of these materials were compared to the widely used linear alkylbenzene sulfonate as incorporated into the same formulations.

The detergent compositions contained 2% carboxymethylcellulose and the silicate content was varied. Sodium acetate and sodium carbonate were investigated as possible reservoirs of alkalinity. Surfactant compatibility with sodium chloride and sodium sulfate was examined. Other additives included trisodium nitrilotriacetate and sodium citrate at moderate levels. Fifteen detergent formulations were screened and the results leave little doubt that acceptable phosphate-free home laundry detergents can be developed.

Abstractor Karl A. Roseman

Institution IIT Research Institute, Chicago, Illinois

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